

# Thermodynamic Description for Concentrated Metallic Solutions Using Interaction Parameters

ZHONGTING MA

The integral molar excess Gibbs energy of a multicomponent system is expressed in terms of interaction parameters, from which the analytical formulae of the activity coefficients of the solutes and solvent, as Eqs. [23] and [24], were deduced. This approach, named the  $\varepsilon$  approach, is able to describe quantitatively the thermodynamic properties of multicomponent systems. It features thermodynamic consistency, high accuracy, and a rather small influence of the higher-interaction parameters on the thermodynamic properties of metallic solutions. A simple modification to the first-order interaction parameters extends the  $\varepsilon$  approach, to be applicable to systems with strong interactions between components at both low and concentrated levels.

## I. INTRODUCTION AND DISCUSSION

THE metal industry has achieved great advances in previous decades in response to the production of high-quality metals. Thermodynamic data such as equilibrium constants and interaction parameters effectively solidify metallurgical fundamentals through an accurate description of the thermodynamics of metallic solutions. This contribution of thermodynamic data to metallurgical fundamentals leads to permanently incremental improvements of metallurgical processes. The present study aims to accurately describe the thermodynamics of metallic solutions using the available thermodynamic parameters.

The interaction-parameter formalism called “Wagner  $\varepsilon$  formalism” is used frequently to express the thermodynamic properties of solutions, particularly of metals, in terms of a MacLaurin series expansion for the logarithm of the activity coefficients of solutes.<sup>[1,2]</sup> Considering a nonreacting solution containing  $N$  components, the MacLaurin series expansion for  $\ln \gamma_i$ , in terms of interaction parameters, is (subscript 1 represents the solvent)

$$\ln \gamma_i = \ln \gamma_i^0 + \sum_{j=2}^N \varepsilon_i^j x_j + \sum_{j=2}^N \rho_i^j x_j^2 + \sum_{j=2}^{N-1} \sum_{k=j+1}^N \rho_i^{jk} x_j x_k + R(x^3) \quad [1]$$

The commonly used Wagner  $\varepsilon$  formalism is the simplest case of a truncated MacLaurin series, *i.e.*, the first-order truncation, because experimental data are not accurate enough to assess interaction parameters beyond the second order. However, a truncated MacLaurin series expansion is thermodynamically inconsistent.<sup>[3,4,5]</sup>

$$\ln \gamma_i = \ln \gamma_i^0 + \sum_{j=2}^N \varepsilon_i^j x_j \quad [2]$$

Equation [2] is for a model where  $\ln \gamma_i$  maintains a linear relation with the composition of the solutes. Numerous experi-

ments on metallic solutions demonstrate that this linear relation between  $\ln \gamma_i$  and  $x_j$  ( $i$  and  $j = 2, 3, \dots, N$ ) holds true over only a modest composition range. For concentrated solutions, the relation is nonlinear. Since higher-order interaction parameters are rarely available, the activity coefficients of solutes at high concentrations have to be calculated using the first-order Wagner  $\varepsilon$  formalism. Significant errors occur between experimental and evaluated data at higher concentrations.<sup>[4,5]</sup> Therefore, the Wagner  $\varepsilon$  formalism is limited to dilute solutions. The thermodynamics of a metallic solution showing a nonlinear relation with its composition has, so far, been not well understood. In view of this, many attempts have been made to develop different approaches to describe the thermodynamics of metallic solutions at both dilute and concentrated levels. The available approaches using interaction parameters are discussed as follows.

### A. Quadratic Formalism and Quasi-Chemical Model

Darken<sup>[3]</sup> and Srikanth and Jacob<sup>[6]</sup> proposed a quadratic formalism that is thermodynamically consistent at both dilute and concentrated levels. (Again, subscript 1 represents the solvent.)

$$\log \gamma_i = \sum_{j=2}^{N-1} \sum_{k=j+1}^N (\alpha_{1j} + \alpha_{1k} - \alpha_{jk}) x_j x_k + \sum_{j=2}^N \alpha_{1j} x_j^2 \text{ (for the solvent)} \quad [3]$$

$$\log \gamma_i = \log \gamma_i^0 + \log \gamma_i^0 - 2\alpha_{1i} x_i - \sum_{j=2}^N \sum_{(j \neq i)} (\alpha_{1i} + \alpha_{1j} - \alpha_{ij}) x_j \text{ (for component } i) \quad [4]$$

The values of the  $\alpha_{ij}$  parameters can be derived from the Wagner  $\varepsilon$  formalism. The quadratic formalism has never enjoyed much popularity, since the published experimental data are mainly presented in terms of the  $\varepsilon$  formalism. The validity of Darken's formalism for multicomponent systems with strong interactions needs further proof.

A quasi-chemical model for dilute ternary and multicomponent systems, first solved by Lupis<sup>[7]</sup> with a formidable

ZHONGTING MA, Associate Professor, formerly with the Beijing University of Science and Technology, Beijing, P.R. China, is with the Institute of Iron and Steel Technology, Freiberg University of Mining and Technology, Freiberg, Germany.

Manuscript submitted January 31, 2000.

mathematical procedure, is very similar to Darken's formalism. Its validity is expected to have a very limited range.

### B. The Unified $\varepsilon$ Formalism

Bale and Pelton<sup>[5,8]</sup> recently proposed a unified  $\varepsilon$  formalism that is thermodynamically consistent at both dilute and concentrated levels. The unified  $\varepsilon$  formalism preserves the simple form of the Wagner  $\varepsilon$  formalism.

$$\ln \gamma_1 = -\frac{1}{2} \sum_{j,k=2}^N \varepsilon_{jk} x_j x_k - \frac{2}{3} \sum_{j,k,l=2}^N \varepsilon_{jkl} x_j x_k x_l - \frac{3}{4} \sum_{j,k,l,m=2}^N \varepsilon_{jklm} x_j x_k x_l x_m - R(x^5) \text{ for the solvent} \quad [5]$$

$$\ln \gamma_i = \ln \gamma_1 + \ln \gamma_i^0 + \sum_{j=2}^N \varepsilon_{ij} x_j + \sum_{j,k=2}^N \varepsilon_{ijk} x_j x_k + \sum_{j,k,l=2}^N \varepsilon_{ijkl} x_j x_k x_l + R(x^4) \text{ for the solute } i \quad [6]$$

The previous two formulae were derived from the molar excess Gibbs energy of a multicomponent solution, which is assumed to be expressed by a Margules-type polynomial expansion.<sup>[9]</sup>

$$\frac{\Delta G^{ex}}{RT} = \sum_{n,m,k,l,\dots=0}^{\infty} \Phi_{nmkl\dots} x_2^n x_3^m x_4^k x_5^l \dots \quad [7]$$

Where  $\Phi_{nmkl\dots}$  are constant coefficients and  $n, m, k$ , and  $j$  are non-negative integers. In their derivation procedure, only compositions near the pure solvent and only terms with  $n = 0$  were considered.<sup>[8]</sup> This consideration obviously makes Eq. [7] impossible to be valid at all compositions. It may limit the applicable composition range of Eqs. [5] and [6], particularly to the systems with strong interactions between components. Moreover, the parameters such as  $\varepsilon_{ij}$  and  $\varepsilon_{ijk}$  are directly related to the constant coefficients  $\Phi_{nmkl\dots}$ , which are mathematically fitting coefficients. It means that the values of the parameters such as  $\varepsilon_{ij}$  and  $\varepsilon_{ijk}$  are obtained through a mathematical fit of the experimental data to Eqs. [5], [6], and/or [7]. The values of these fitting coefficients are generally different from those of the available interaction parameters. For example, the values of  $\varepsilon_{Fe}^{Fe} = 1.92$ ,  $\varepsilon_{Cr}^{Cr} = 1.85$ , and  $\varepsilon_{Cr}^{Fe} = 2.19$  for the Ni-Fe-Cr melts at 1873 K were obtained from the experimental data of Gibly and Pierre,<sup>[10]</sup> while the different values were fitted by the unified  $\varepsilon$  approach with the same experimental data:<sup>[5]</sup>  $\varepsilon_{FeFe} = 2.3202$ ,  $\varepsilon_{CrCr} = 1.5828$ , and  $\varepsilon_{FeCr} = 5.2785$ . These fitting coefficients are also normally dependent on the components from a mathematical point of view. Therefore, it is hard to guarantee the consistency, in theory, between the values of the fitting coefficients obtained from a solution with less components and those obtained from a solution with more components. That is, the values of the fitting coefficients obtained from solutions with less components and those with more components are not the same. For example,  $\varepsilon_{AB}$  and  $\varepsilon_{ABB}$ , deduced from the ternary system M-A-B, are not identical to the values obtained from the quaternary M-A-B-C or pentenary M-A-B-C-D systems, etc. A good applicability of this approach is reached,<sup>[8]</sup> because of the introduction of numerical relations between interaction parameters and fitting coefficients such as  $\varepsilon_{ij} = \varepsilon_i^j$ .

### C. Modified MacLaurin Infinite Series

Hajra *et al.*<sup>[11,12,13]</sup> deduced the functions of activity coefficients with compositions in the ternary system based on the MacLaurin infinite series, which is expressed in terms of the molar excess Gibbs energy subject to appropriate boundary conditions. For their model,

$$\ln \gamma_i = \sum_{j=2}^3 \varepsilon_j^i (x_j + \ln(1 - x_j)) - \varepsilon_2^3 \ln \frac{(1 - x_2)(1 - x_3)}{1 - x_2 - x_3} \quad [8]$$

$$\ln \gamma_i = \ln \gamma_i^0 + \sum_{j=2}^3 \varepsilon_j^i x_j + (\varepsilon_k^k - \varepsilon_k^i) \ln(1 - x_k) \quad (k \text{ and } i = 2 \text{ and } 3 \text{ and } k \neq i) \quad [9]$$

These expressions maintain thermodynamic consistency. However, its applicability must be tested by more ternary systems than the Ni-Fe-Cr system, as suggested by Pelton.<sup>[14]</sup> Moreover, this approach is hardly extended to a multicomponent metallic solution.

In the present article, a new method is proposed to describe the thermodynamic properties of multicomponent systems. It is thermodynamically consistent and independent of integration paths. Furthermore, examples are presented to show that the present approach gives more accuracy than the available approaches such as the Wagner  $\varepsilon$  formalism, the unified  $\varepsilon$  formalism, and the Hajra-Frohberg's approach.

## II. THERMODYNAMIC PARAMETERS AND THE NATURE OF METALLIC SOLUTIONS

The concept of activity was introduced by Lewis in 1913. The definition of the activity of component  $i$  in a solution is the ratio of the fugacity of  $i$  in the solution to that of pure  $i$  in its standard state.

$$a_i \equiv \frac{\hat{f}_i}{\hat{f}_i^0} \quad [10]$$

It is common to take  $\hat{f}_i^0 = 1$  bar as the standard state when  $i$  is gaseous. When  $i$  is in a condensed phase, it is often to be chosen as the standard state of the pure component  $i$  at 1 bar pressure and in a precisely defined aggregation state.

Fugacity expresses the tendency of a component to escape from a medium. This physical quantity was also introduced by Lewis in 1901. The fugacity of  $i$  in a condensed phase is defined by the fugacity of its vapor at equilibrium. In practice, the fugacity of component  $i$  is assumed to be equal its pressure, as the fugacity is well below 1 bar. Thus, the activity of component  $i$  in the solution can be expressed as

$$a_i \equiv \frac{\hat{f}_i}{\hat{f}_i^0} \approx \frac{p_i}{p_i^0} \quad [11]$$

Therefore, the activity is the ability of a component to escape from the solution. The volatile elements in a solution always demonstrate higher activities in comparison with the inertial elements at the same concentration.

The activity coefficient is defined by

$$\gamma_i \equiv \frac{\hat{f}_i}{\hat{f}_i^{\text{ideal}}} \equiv \frac{\hat{f}_i}{x_i \hat{f}_i^0} \equiv \frac{a_i}{x_i} \approx \frac{p_i}{x_i p_i^0} \quad [12]$$

It indicates that the activity coefficient of  $i$  ( $\gamma_i$ ) represents the deviation ratio of its fugacity and ideal fugacity. The

activity and activity coefficient are directly related to the nature of atoms, ions, and their interactions. The activity and activity coefficient of  $i$  tend to decrease if the other atoms and ions in the solution finally attract the species  $i$  (atom or ion) or hinder its escape. Many solution models<sup>[15]</sup> such as the regular, conformal, hard-sphere, and quasi-crystalline model were developed, intending to reveal the relation between thermodynamic parameters such as the activity and activity coefficient and the nature and interactions of atoms and ions. For example, a strictly regular solution model gives the following relation for a binary  $\alpha$ - $\beta$  solution:

$$\ln \gamma_\alpha = RTw_{\alpha\beta}x_\beta^2 \quad [13]$$

$$\ln \gamma_\beta = RTw_{\alpha\beta}x_\alpha^2 \quad [14]$$

where  $w_{\alpha\beta}$  is the energy parameter.

$$w_{\alpha\beta} = zN_A \left( u_{\alpha\beta} - \frac{1}{2} u_{\alpha\alpha} - \frac{1}{2} u_{\beta\beta} \right) \quad [15]$$

where  $z$  is the coordination number;  $N_A$  is the Avogadro number; and  $u_{\alpha\beta}$ ,  $u_{\alpha\alpha}$ , and  $u_{\beta\beta}$  are the pair potential energies or bond energies. Modifications to the strictly regular solutions were made for considering the cohesion energy of metals in terms of the valence-bond theory of molecules,<sup>[16,17]</sup> coordination-number dependency of concentration,<sup>[18,19]</sup> and so on.<sup>[15]</sup> Based on the aforementioned concept, *i.e.*, that the activity and activity coefficient are directly related to the nature of metallic solutions, the developed solution models were used more recently to evaluate thermodynamic parameters such as interaction parameters instead of traditionally experimental determinations.<sup>[20,21,22]</sup> It is worth mentioning that the accuracy and reliability need to be further improved for the theoretical evaluations, because of the lack of a basic understanding of liquid metallic solutions.

### III. ESTABLISHMENT OF FORMALISM

For a nonreacting solution containing  $N$  components at a fixed temperature and pressure, its integral molar excess Gibbs energy is a state function of the composition of the solution.

$$G^{ex} = g(x_2, x_3, x_4, \dots, x_N) \quad [16]$$

The Taylor expansion, referring to an infinitely dilute solution, is valid for this function.

$$\begin{aligned} \Delta G^{ex} = (\Delta G^{ex})_{x_1 \rightarrow 1} &+ \sum_{i=2}^N \sum_{n_1=1}^{\infty} \frac{1}{n_1!} \left( \frac{\partial^{n_1} \Delta G^{ex}}{\partial x_1^{n_1}} \right)_{x_1 \rightarrow 1} x_1^{n_1} \\ &+ \sum_{i=2}^{N-1} \sum_{j=i+1}^N \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{1}{n_1! n_2!} \left( \frac{\partial^{n_1+n_2} \Delta G^{ex}}{\partial x_1^{n_1} \partial x_j^{n_2}} \right)_{x_1 \rightarrow 1} x_1^{n_1} x_j^{n_2} + \dots \end{aligned} \quad [17]$$

The molar excess Gibbs energy ( $\Delta G^{ex}$ ) meets the following general and boundary conditions:

- (1) General condition:  $x_1 \rightarrow 1, x_j \rightarrow 0$  ( $j = 2, 3, \dots, N$ )  $\Rightarrow \Delta G^{ex} \rightarrow 0$
- (2) Boundary conditions:  $x_i \rightarrow 1, x_j \rightarrow 0$  ( $i, j = 2, 3, \dots, N; i \neq j$ )  $\Rightarrow \Delta G^{ex} \rightarrow 0$

After inserting the previous conditions into the series [17], the following equation is obtained:

$$\sum_{n=1}^{\infty} \frac{1}{n!} \left( \frac{\partial^n \Delta G^{ex}}{\partial x_1^n} \right)_{x_1 \rightarrow 1} = 0 \quad [18]$$

Substituting Eq. [18] into Eq. [17] yields

$$\begin{aligned} \Delta G^{ex} = & - \sum_{j=2}^N \sum_{n_1=1}^{\infty} (1 - x_j^{n_1}) \frac{1}{n_1!} \left( \frac{\partial^{n_1} \Delta G^{ex}}{\partial x_j^{n_1}} \right)_{x_1 \rightarrow 1} \\ & + \sum_{i=2}^{N-1} \sum_{j=i+1}^N \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{1}{n_1! n_2!} \left( \frac{\partial^{n_1+n_2} \Delta G^{ex}}{\partial x_i^{n_1} \partial x_j^{n_2}} \right)_{x_1 \rightarrow 1} x_i^{n_1} x_j^{n_2} + \dots \\ = & \sum_{j=2}^N x_j (1 - x_j) \left( \left( \frac{\partial \Delta G^{ex}}{\partial x_j} \right)_{x_1 \rightarrow 1} + \sum_{n=1}^{\infty} \left( x_j^n \sum_{k=1}^{n+1} \frac{1}{k!} \left( \frac{\partial^k \Delta G^{ex}}{\partial x_j^k} \right)_{x_1 \rightarrow 1} \right) \right) \\ & + \sum_{i=2}^{N-1} \sum_{j=i+1}^N \sum_{n_1=1}^{\infty} \sum_{n_2=1}^{\infty} \frac{1}{n_1! n_2!} \left( \frac{\partial^{n_1+n_2} \Delta G^{ex}}{\partial x_i^{n_1} \partial x_j^{n_2}} \right)_{x_1 \rightarrow 1} x_i^{n_1} x_j^{n_2} + \dots \end{aligned} \quad [19]$$

The partial molar excess Gibbs energy can be written as Eq. [20] after introducing interaction parameters, as defined in Table I, neglecting all of the higher-order terms that are listed in Table II. This neglect takes into account that higher-order interaction parameters are not available and that the accuracy of results from high-temperature experimental techniques is limited.

$$\begin{aligned} \frac{\Delta G^{ex}}{RT} = & \sum_{j=2}^N (1 - x_j) x_j \left( \ln \gamma_j^0 (1 + \sum_{n=1}^{\infty} x_j^n) + \sum_{n=1}^{\infty} \epsilon_j^n \left( 1 - \frac{1}{n+1} \right) x_j^n \right) \\ & + \sum_{j=2}^{N-1} \sum_{k=j+1}^N x_j x_k \left( \epsilon_{jk}^1 + \epsilon_{jk}^2 \sum_{n=1}^{\infty} \frac{x_k^n}{n+1} + \epsilon_{jk}^3 \sum_{n=1}^{\infty} \frac{x_j^n}{n+1} \right) \\ & + \sum_{j=2}^{N-1} \sum_{k=j+1}^N \frac{\epsilon_{jk}^2}{2} x_j^2 x_k^2 \left( 1 - \sum_{n=2}^{\infty} (x_j^n + x_k^n) \right) \end{aligned} \quad [20]$$

With progression functions, the previous equation can be rewritten as

$$\begin{aligned} \frac{\Delta G^{ex}}{RT} = & \sum_{j=2}^N x_j (1 - x_j) \left( \frac{1}{1 - x_j} \ln \gamma_j^0 + \epsilon_j^1 \left( \frac{1}{1 - x_j} + \frac{\ln(1 - x_j)}{x_j} \right) \right) \\ & - \sum_{j=2}^{N-1} \sum_{k=j+1}^N x_j x_k \epsilon_{jk}^1 \left( 1 + \frac{\ln(1 - x_j)}{x_j} + \frac{\ln(1 - x_k)}{x_k} \right) \\ & + \frac{1}{2} \sum_{j=2}^{N-1} \sum_{k=j+1}^N \epsilon_{jk}^2 x_j^2 x_k^2 \left( \frac{1}{1 - x_j} + \frac{1}{1 - x_k} - 1 \right) \end{aligned} \quad [21]$$

The partial molar Gibbs energy can be calculated from the molar Gibbs energy according to the following equation:

$$\frac{\Delta G_i^{ex}}{RT} = \frac{\Delta G^{ex}}{RT} + \frac{1}{RT} \sum_{j=2}^N (\delta_{ij} - x_j) \frac{\partial \Delta G^{ex}}{\partial x_j} \quad [22]$$

where  $\delta_{ij}$  is the Kronecker delta, zero for  $i \neq j$  and 1 for  $i = j$ .

According to Eq. [22] and  $\ln \gamma_i = \Delta G_i^{ex}/RT$ , the expression for  $\ln \gamma_1$  (where 1 represents the solvent) and  $\ln \gamma_i$  (where  $i$  is a solute component) can be derived from Eq. [21].

**Table I. Relation between Derivatives of the Excess Gibbs Free Energy and the Conventional Interaction Parameters**

Number	Relations
1	$\frac{1}{RT} \left( \frac{\partial \Delta G^{ex}}{\partial x_j} \right)_{x_1 \rightarrow 1} = \ln \gamma_j^0$
2	$\frac{1}{RT} \left( \frac{\partial^2 \Delta G^{ex}}{\partial x_j^2} \right)_{x_1 \rightarrow 1} = \varepsilon_j^j$
3	$\frac{1}{RT} \left( \frac{\partial^3 \Delta G^{ex}}{\partial x_j^3} \right)_{x_1 \rightarrow 1} = \varepsilon_j^j + 2\rho_j^j$
4	$\frac{1}{RT} \left( \frac{\partial^n \Delta G^{ex}}{\partial x_j^n} \right)_{x_1 \rightarrow 1} = (n-2) \left( \frac{\partial^{n-1} \Delta G^{ex}}{\partial x_j^{n-1}} \right)_{x_1 \rightarrow 1} + J_{jj}^{(n-1)}, \quad n > 3$
5	$\frac{1}{RT} \left( \frac{\partial^2 \Delta G^{ex}}{\partial x_k \partial x_j} \right)_{x_1 \rightarrow 1} = \varepsilon_k^j$
6	$\frac{1}{RT} \left( \frac{\partial^3 \Delta G^{ex}}{\partial x_k^2 \partial x_j} \right)_{x_1 \rightarrow 1} = \varepsilon_k^j + \rho_k^{jk}$
7	$\frac{1}{RT} \left( \frac{\partial^n \Delta G^{ex}}{\partial x_k^{n-1} \partial x_j} \right)_{x_1 \rightarrow 1} = (n-2) \left( \frac{\partial^{n-2} \Delta G^{ex}}{\partial x_k^{n-2} \partial x_j} \right)_{x_1 \rightarrow 1} + J_{jk}^{(n-1)} \quad (n > 3)$
8	$\frac{1}{RT} \left( \frac{\partial^{n_1+n_2} \Delta G^{ex}}{\partial x_j^{n_1} \partial x_k^{n_2}} \right)_{x_1 \rightarrow 1} = (n_1+n_2-2) \left( \frac{\partial^{n_1+n_2-1} \Delta G^{ex}}{\partial x_j^{n_1-1} \partial x_k^{n_2}} \right)_{x_1 \rightarrow 1} + J_{jk}^{(n_1+n_2-1)} \quad (n_1, n_2 > 3)$

Here,  $\varepsilon$  and  $\rho$  are first- and second-order activity interaction parameters, respectively, and their subscripts and superscripts are the same as those designed by Lupis and Elliott.<sup>[2]</sup> The  $J$  denotes higher-order interaction parameters.

**Table II. The Neglect of the Impact Terms in Equation [19]**

Number	Terms
1	the second-order and higher-order interaction parameters
2	$\left( \frac{\partial^{n_1+n_2+n_3} \Delta G^{ex}}{\partial x_i^{n_1} \partial x_j^{n_2} \partial x_k^{n_3}} \right)_{x_1 \rightarrow 1}$ and analogous derivations with more components
3	$\left( \frac{\partial^{n_1+n_2} \Delta G^{ex}}{\partial x_i^{n_1} \partial x_j^{n_2}} \right)_{x_1 \rightarrow 1}$ for $n_1 \geq 3$ and $n_2 \geq 3$

$$\begin{aligned}
\ln \gamma_i &= \ln \gamma_i + \frac{1}{RT} \frac{\partial \Delta G^{ex}}{\partial x_i} \\
&= \ln \gamma_i + \ln \gamma_i^0 - \varepsilon_i^i \ln(1-x_i) \\
&\quad - \sum_{\substack{k=2 \\ (k \neq i)}}^N \varepsilon_i^k x_k \left( 1 + \frac{\ln(1-x_k)}{x_k} - \frac{1}{1-x_i} \right) \\
&\quad + \sum_{\substack{k=2 \\ (k \neq i)}}^N \varepsilon_i^k x_k^2 x_i \left( \frac{1}{1-x_i} + \frac{1}{1-x_k} + \frac{x_i}{2(1-x_i)^2} - 1 \right) \quad [24]
\end{aligned}$$

$$\begin{aligned}
\ln \gamma_i &= \frac{\Delta G^{ex}}{RT} - \frac{1}{RT} \sum_{i=2}^N x_i \frac{\partial \Delta G^{ex}}{\partial x_i} \\
&= \sum_{i=2}^N \varepsilon_i^i (x_i + \ln(1-x_i)) - \sum_{j=2}^{N-1} \sum_{k=j+1}^N \\
&\quad \varepsilon_j^k x_j x_k \left( 1 + \frac{\ln(1-x_j)}{x_j} + \frac{\ln(1-x_k)}{x_k} \right) \\
&\quad + \sum_{i=2}^N \sum_{\substack{k=2 \\ (k \neq i)}}^N \varepsilon_i^k x_i x_k \left( 1 + \frac{\ln(1-x_k)}{x_k} - \frac{1}{1-x_i} \right) \\
&\quad + \frac{1}{2} \sum_{j=2}^{N-1} \sum_{k=j+1}^N \varepsilon_j^k x_j^2 x_k^2 \left( \frac{1}{1-x_j} + \frac{1}{1-x_k} - 1 \right) \\
&\quad - \sum_{i=2}^N \sum_{\substack{k=2 \\ (k \neq i)}}^N \varepsilon_i^k x_i^2 x_k^2 \left( \frac{1}{1-x_i} + \frac{1}{1-x_k} + \frac{x_i}{2(1-x_i)^2} - 1 \right) \quad [23]
\end{aligned}$$

Equations [23] and [24] express the activity coefficients of the solvent and solutes, respectively, for multicomponent metallic solutions, in terms of first-order interaction parameters, on the basis of mole fractions. These expressions are thermodynamically consistent with the Gibbs–Duhem equation and other thermodynamic relations. The constants  $\varepsilon_i^j$  in Eqs. [23] and [24] are the same as the interaction parameters introduced by Wagner,<sup>[1,2]</sup> having the strict physical meaning defined in Table I. In addition, examples are presented in the following section to demonstrate that the calculations based on Eqs. [23] and [24] result in a higher accuracy in comparison with the available approaches. Equations [23] and [24] reduce to Eqs. [25] and [26], respectively, in the special case of ternary systems. The present  $\varepsilon$  approach coincides with the Wagner  $\varepsilon$  formalism in the case of the binary systems.<sup>[23]</sup>

$$\begin{aligned}
\ln \gamma_1 &= \varepsilon_2^2 (x_2 + \ln(1-x_2)) + \varepsilon_3^3 (x_3 + \ln(1-x_3)) \\
&\quad + \varepsilon_2^3 x_2 x_3 \left( 1 - \frac{1}{1-x_2} - \frac{1}{1-x_3} \right)
\end{aligned}$$

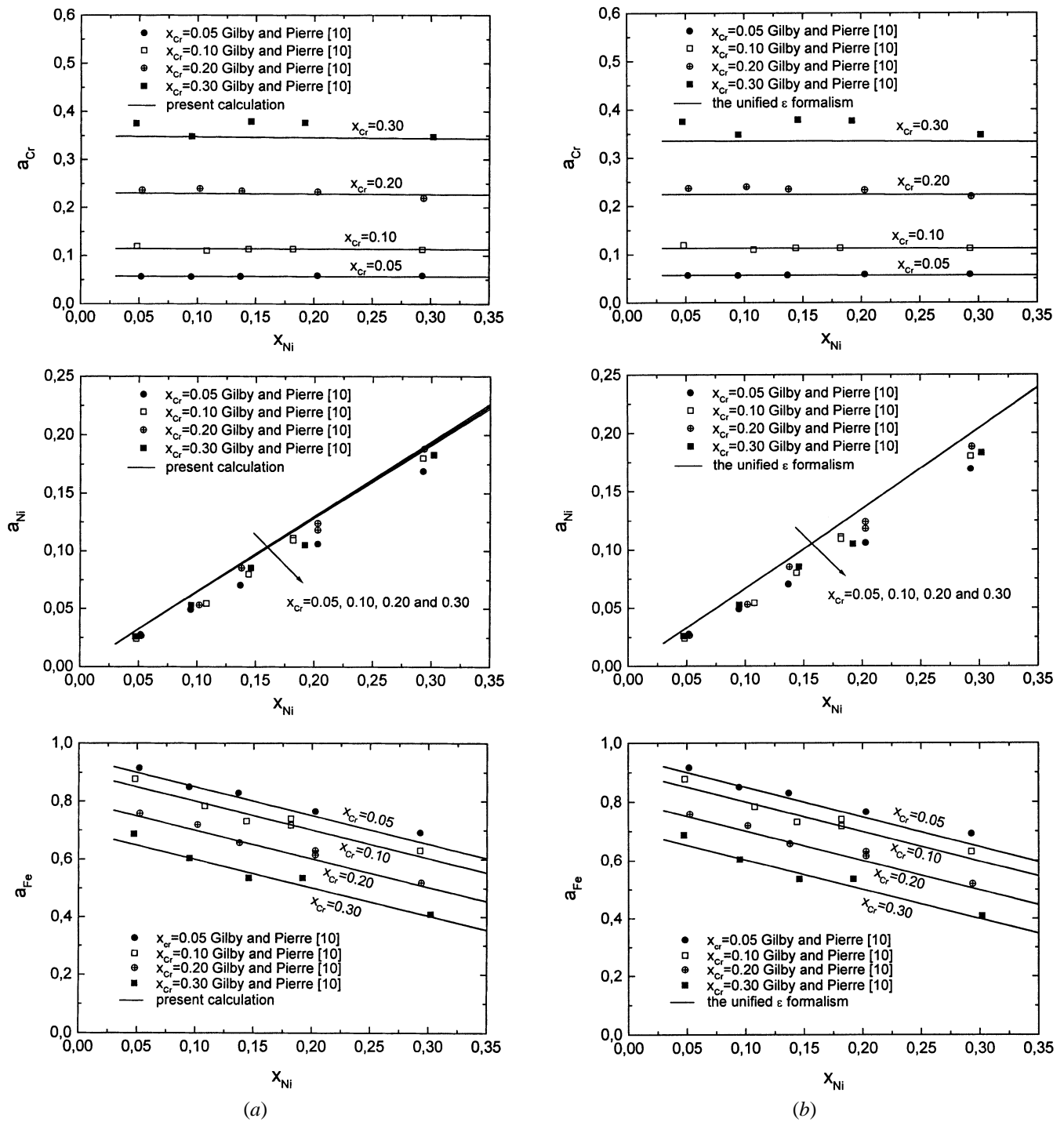


Fig. 1—(a) Comparison of the calculated with experimental results for Fe-Cr-Ni melts at 1873 K (the calculated results are obtained by the present  $\varepsilon$  approach). (b) Comparison of the calculated with experimental results for Fe-Cr-Ni melts at 1873 K (the calculated results are obtained by the unified  $\varepsilon$  formalism).

$$-\frac{\varepsilon_2^3}{2}x_2^2x_3^2\left(\frac{3}{1-x_2}+\frac{3}{1-x_3}+\frac{x_2}{(1-x_2)^2}+\frac{x_3}{(1-x_3)^2}-3\right) \quad [25]$$

$$\ln \gamma_i = \ln \gamma_1 + \frac{1}{RT} \frac{\partial \Delta G^{ex}}{\partial x_i} = \ln \gamma_1 + \ln \gamma_i^0 - \varepsilon_i^i \ln(1-x_i)$$

$$-\varepsilon_i^k x_k \left(1 + \frac{\ln(1-x_k)}{x_k} - \frac{1}{1-x_i}\right)$$

$$+\varepsilon_i^k x_k^2 x_i \left(\frac{1}{1-x_i} + \frac{1}{1-x_k} + \frac{x_i}{2(1-x_i)^2} - 1\right)$$

$$(i \text{ and } k = 2 \text{ and } 3 \text{ and } k \neq i)$$

$$[26]$$

#### IV. EXAMPLES AND DISCUSSION

In this section, the results calculated by different approaches such as the present  $\varepsilon$  approach, the Wagner  $\varepsilon$  formalism, the

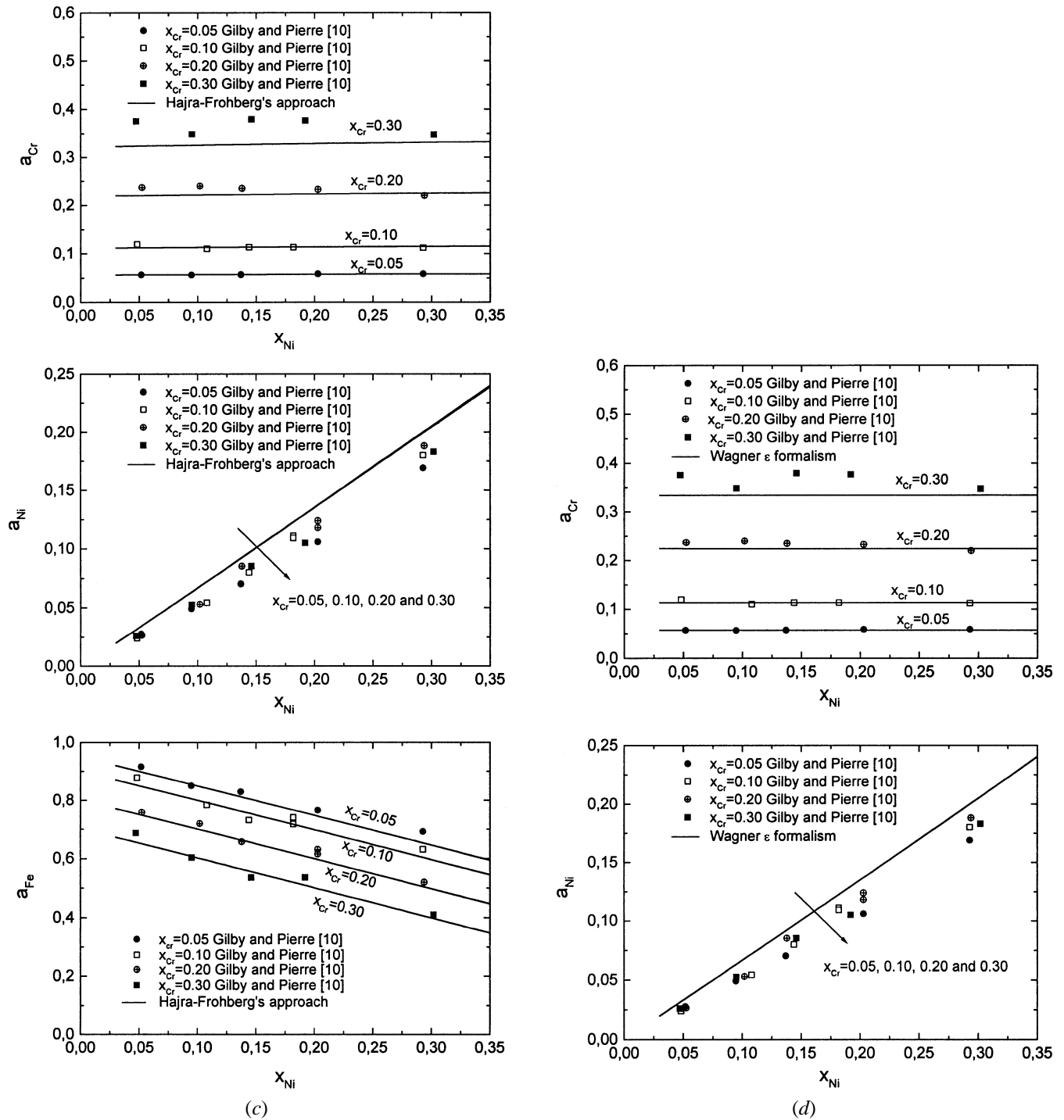


Fig. 1—Continued (c) Comparison of the calculated with experimental results for Fe-Cr-Ni melts at 1873 K (the calculated results are obtained by Hajra-Frohberg's approach). (d) Comparison of the calculated with experimental results for Fe-Cr-Ni melts at 1873 K (the calculated results are obtained by Wagner  $\epsilon$  formalism).

unified  $\epsilon$  formalism, and the Hajra-Frohberg approach will be compared with experimental data for metal melts.

#### A. Fe-Cr-Ni and Ni-Cr-Fe Systems at 1873 K

In Figures 1(a) through (d) the calculated results with the aforementioned approaches are plotted against experimental results<sup>[10]</sup> for the activities of the solvent and solutes in Fe-Cr-Ni melts at 1873 K. The present  $\epsilon$  approach evaluates

the activities of Fe, Cr, and Ni in Fe-Cr-Ni melts at 1873 K according to the following equations, which are deduced from Eqs. [23] and [24].

$$\ln \gamma_{Fe} = \epsilon_{Cr}^{Cr}(x_{Cr} + \ln(1 - x_{Cr})) + \epsilon_{Ni}^{Ni}(x_{Ni} + \ln(1 - x_{Ni})) + \epsilon_{Cr}^{Ni}x_{Cr}x_{Ni}\left(1 - \frac{1}{1 - x_{Cr}} - \frac{1}{1 - x_{Ni}}\right)$$

$$-\frac{\varepsilon_{\text{Ni}}^{\text{Cr}}}{2}x_{\text{Cr}}^2x_{\text{Ni}}^2\left(\frac{3}{1-x_{\text{Cr}}}+\frac{3}{1-x_{\text{Ni}}}+\frac{x_{\text{Cr}}}{(1-x_{\text{Cr}})^2}+\frac{x_{\text{Ni}}}{(1-x_{\text{Ni}})^2}-3\right)[27]$$

$$\begin{aligned}\ln \gamma_{\text{Cr}} &= \ln \gamma_{\text{Fe}} + \ln \gamma_{\text{Cr}}^0 - \varepsilon_{\text{Cr}}^{\text{Cr}} \ln(1-x_{\text{Cr}}) \\ &- \varepsilon_{\text{Cr}}^{\text{Ni}} x_{\text{Ni}} \left(1 + \frac{\ln(1-x_{\text{Ni}})}{x_{\text{Ni}}} - \frac{1}{1-x_{\text{Cr}}}\right) \\ &+ \varepsilon_{\text{Cr}}^{\text{Ni}} x_{\text{Ni}}^2 x_{\text{Cr}} \left(\frac{1}{1-x_{\text{Cr}}} + \frac{1}{1-x_{\text{Ni}}} + \frac{x_{\text{Cr}}}{2(1-x_{\text{Cr}})^2} - 1\right)\end{aligned}\quad [28]$$

$$\begin{aligned}\ln \gamma_{\text{Ni}} &= \ln \gamma_{\text{Fe}} + \ln \gamma_{\text{Ni}}^0 - \varepsilon_{\text{Ni}}^{\text{Ni}} \ln(1-x_{\text{Ni}}) \\ &- \varepsilon_{\text{Ni}}^{\text{Cr}} x_{\text{Cr}} \left(1 + \frac{\ln(1-x_{\text{Cr}})}{x_{\text{Cr}}} - \frac{1}{1-x_{\text{Ni}}}\right) \\ &+ \varepsilon_{\text{Ni}}^{\text{Cr}} x_{\text{Cr}}^2 x_{\text{Ni}} \left(\frac{1}{1-x_{\text{Ni}}} + \frac{1}{1-x_{\text{Cr}}} + \frac{x_{\text{Ni}}}{2(1-x_{\text{Ni}})^2} - 1\right)\end{aligned}\quad [29]$$

The Wagner  $\varepsilon$  formalism predicts the activities according to the following equations. However, the activity of the solvent Fe cannot be evaluated by the Wagner  $\varepsilon$  formalism.

$$\ln \gamma_{\text{Cr}} = \ln \gamma_{\text{Cr}}^0 + \varepsilon_{\text{Cr}}^{\text{Cr}} x_{\text{Cr}} + \varepsilon_{\text{Cr}}^{\text{Ni}} x_{\text{Ni}} \quad [30]$$

$$\ln \gamma_{\text{Ni}} = \ln \gamma_{\text{Ni}}^0 + \varepsilon_{\text{Ni}}^{\text{Ni}} x_{\text{Ni}} + \varepsilon_{\text{Ni}}^{\text{Cr}} x_{\text{Cr}} \quad [31]$$

The unified  $\varepsilon$  formalism assesses the activities in light of Eqs. [32] through [34].

$$\ln \gamma_{\text{Fe}} = -\frac{1}{2}(\varepsilon_{\text{CrCr}}x_{\text{Cr}}^2 + 2\varepsilon_{\text{CrNi}}x_{\text{Cr}}x_{\text{Ni}} + \varepsilon_{\text{NiNi}}x_{\text{Ni}}^2) \quad [32]$$

$$\ln \gamma_{\text{Cr}} = \ln \gamma_{\text{Fe}} + \ln \gamma_{\text{Cr}}^0 + \varepsilon_{\text{CrCr}}x_{\text{Cr}} + \varepsilon_{\text{CrNi}}x_{\text{Ni}} \quad [33]$$

$$\ln \gamma_{\text{Ni}} = \ln \gamma_{\text{Fe}} + \ln \gamma_{\text{Ni}}^0 + \varepsilon_{\text{NiNi}}x_{\text{Ni}} + \varepsilon_{\text{NiCr}}x_{\text{Cr}} \quad [34]$$

Hajra-Frohberg's approach estimates the activities on basis of the following equations:

$$\begin{aligned}\ln \gamma_{\text{Fe}} &= \varepsilon_{\text{Cr}}^{\text{Cr}}(x_{\text{Cr}} + \ln(1-x_{\text{Cr}})) + \varepsilon_{\text{Ni}}^{\text{Ni}}(x_{\text{Ni}} + \ln(1-x_{\text{Ni}})) \\ &- \varepsilon_{\text{Cr}}^{\text{Ni}} \ln \frac{(1-x_{\text{Cr}})(1-x_{\text{Ni}})}{1-x_{\text{Cr}}-x_{\text{Ni}}}\end{aligned}\quad [35]$$

$$\ln \gamma_{\text{Cr}} = \ln \gamma_{\text{Cr}}^0 + \varepsilon_{\text{Cr}}^{\text{Cr}}x_{\text{Cr}} + \varepsilon_{\text{Ni}}^{\text{Ni}}x_{\text{Ni}} + (\varepsilon_{\text{Ni}}^{\text{Ni}} - \varepsilon_{\text{Cr}}^{\text{Ni}})\ln(1-x_{\text{Ni}}) \quad [36]$$

$$\ln \gamma_{\text{Ni}} = \ln \gamma_{\text{Ni}}^0 + \varepsilon_{\text{Ni}}^{\text{Ni}}x_{\text{Ni}} + \varepsilon_{\text{Cr}}^{\text{Cr}}x_{\text{Cr}} + (\varepsilon_{\text{Cr}}^{\text{Cr}} - \varepsilon_{\text{Cr}}^{\text{Ni}})\ln(1-x_{\text{Cr}}) \quad [37]$$

All the calculations are based on the first-order interaction parameters  $e_{\text{Cr}}^{\text{Cr}} = -0.00067$ ,<sup>[24]</sup>  $e_{\text{Ni}}^{\text{Ni}} = 0.0007$ ,<sup>[25]</sup>  $e_{\text{Cr}}^{\text{Ni}} = 0.00022$ ,<sup>[25]</sup> and the activity coefficients at infinite dilution,  $\gamma_{\text{Ni}}^0 = 0.66$ ,<sup>[25]</sup> and  $\gamma_{\text{Cr}}^0 = 1.14$ .<sup>[25]</sup> Interaction parameters based on a mole fraction can be obtained using the following conversion formula:<sup>[25]</sup>

$$\varepsilon_i^j = \frac{M_j}{M_i}(230e_j^i - 1) + 1 \quad [38]$$

where  $M_j$  and  $M_i$  represent the atomic weight of solute  $j$  and solvent  $i$ , respectively.

It is obvious that the four different approaches give almost the same accuracy to describe the Fe-Cr-Ni system at 1873 K. The term  $\ln \gamma_j$  ( $j$  is the solute) shows a linear relation with the mole fractions of solutes. In this linear-relation range,

the four approaches tend to reach identical results. Gibby and Pierre<sup>[10]</sup> experimentally determined the first-order interaction parameters and the activity coefficients at infinite dilution for Ni-based Cr-Fe melts at 1873 K. These parameters are  $\varepsilon_{\text{Cr}}^{\text{Cr}} = 1.85$ ,  $\varepsilon_{\text{Fe}}^{\text{Fe}} = 1.92$ ,  $\varepsilon_{\text{Cr}}^{\text{Fe}} = 2.19$ ,  $\gamma_{\text{Fe}}^0 = 0.40$ , and  $\gamma_{\text{Cr}}^0 = 0.46$ . Figures 2(a) through (d) numerically show the calculated and experimental results for Ni-Cr-Fe (Ni is the solvent) melts at 1873 K. It is found that the present approach gives more accuracy in describing the Ni-Cr-Fe system at 1873 K in comparison with other approaches.

### B. Fe-C<sub>Sat</sub>-j System at 1823 K

It is found experimentally that the solubility of C in Fe- $j$  melts has a close relation to the content of  $j$ . This relation at constant temperature can be expressed as<sup>[26]</sup>

$$\begin{aligned}[\text{pct C}]_{\text{max}} &= [\text{pct C}]'_{\text{max}} + m [\text{pct } j] \\ &+ s [\text{pct } j]^2 + \dots\end{aligned}\quad [39]$$

where  $[\text{pct C}]_{\text{max}}$  and  $[\text{pct C}]'_{\text{max}}$  represent the solubility of C in Fe- $j$  melts and in liquid iron, respectively;  $m$  and  $s$  are the first- and second-order solubility parameters.

Neumann and Schenck<sup>[26]</sup> experimentally determined the content range of element  $j$ , in which  $[\text{pct C}]_{\text{max}}$  shows a linear relation with  $[\text{pct } j]$  for Fe-C- $j$  melts. Table III gives some of their results. The system Fe-C was intensively investigated, and the reported values of  $e_{\text{C}}^{\text{C}}$  from different sources show a little difference. The value of  $e_{\text{C}}^{\text{C}}$  in liquid iron at 1823 K was reported as  $358/T$ <sup>[27]</sup> (0.20 at 1823 K),  $246/T + 0.008$ <sup>[28]</sup> (0.14),  $158/T + 0.058$ <sup>[29]</sup> (0.15), 0.20,<sup>[30]</sup> and 0.25.<sup>[31]</sup> The average value of  $e_{\text{C}}^{\text{C}} = 0.19$ , i.e.,  $e_{\text{C}}^{\text{C}} = 10.182$  at 1823 K, is used in the present calculations. The activity coefficient at infinite dilution of  $\gamma_{\text{C}}^0$  equals 0.599 at 1823 K.<sup>[32]</sup> The first-order interaction parameters of  $\varepsilon_{\text{C}}^j$  and  $\varepsilon_j^{\text{C}}$  are listed in Table IV. Based on these parameters, the solubility of C in Fe- $j$  melts can be calculated. Figures 3 through 8 compare the calculated and experimental results. It is obvious that the present  $\varepsilon$  approach, together with the Wagner  $\varepsilon$  formalism, are suitable to perform thermodynamic analysis for Fe-C- $j$  melts. For testing the applicability of the present  $\varepsilon$  approach to the systems with strong interactions between components, the following calculations are performed. The presently used thermodynamic parameters are listed in Table V.

### C. Calcium in Iron-Based Melts

Ca is widely employed to treat liquid steel. Dissolved Ca in steel melts directly influences the efficiency of Ca treatment. Experimental results<sup>[33–37]</sup> show that the elements Al, Ni, and Si increase the solubility of Ca in iron melts, but Cr decreases it. The calculated maximum Ca content in the Fe- $j$  melts at 1873 K is shown as a function of the content of solute  $j$  in Figures 9 through 13, in which the experimental data are also presented. It is concluded that the calculations based on the present  $\varepsilon$  approach are in good agreement with the experimental results. The calculated maximum Ca content is obtained under  $a_{\text{Ca}} = 0.8$ , because of the formation of liquid Ca-CaO mixtures on the top of the melts.<sup>[33,35]</sup> Table VI<sup>[35]</sup> shows that the dissolved Fe,  $j$ , and CaO in the liquid Ca phase vary with the content of  $j$  in iron melts. The deviation of the calculated results from the experimental

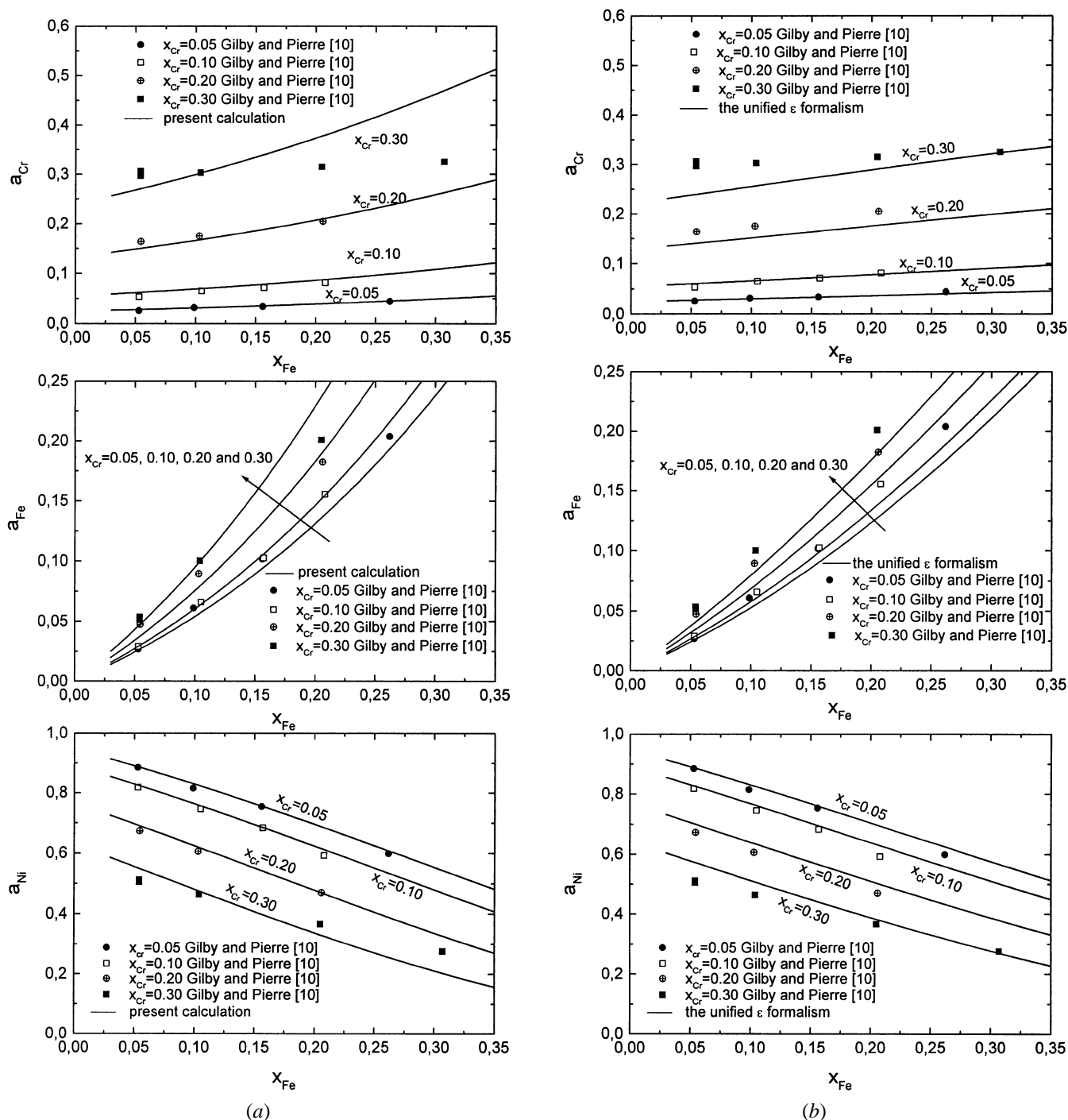


Fig. 2—Continued (a) Comparison of the calculated with experimental results for Ni-Cr-Fe melts at 1873 K (the calculated results are obtained by the present  $\varepsilon$  approach). (b) Comparison of the calculated with experimental results for Ni-Cr-Fe melts at 1873 K (the calculated results are obtained by the unified  $\varepsilon$  formalism).

ones is probably caused by a transfer of the third element  $j$  from the Fe- $j$  melt to the Ca phase. This causes a decrease of Ca activity, which was proven and discussed in the article by Köhler *et al.*<sup>[33]</sup>

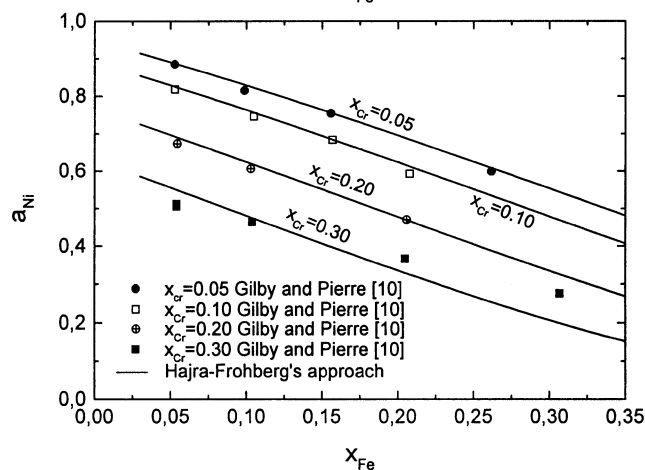
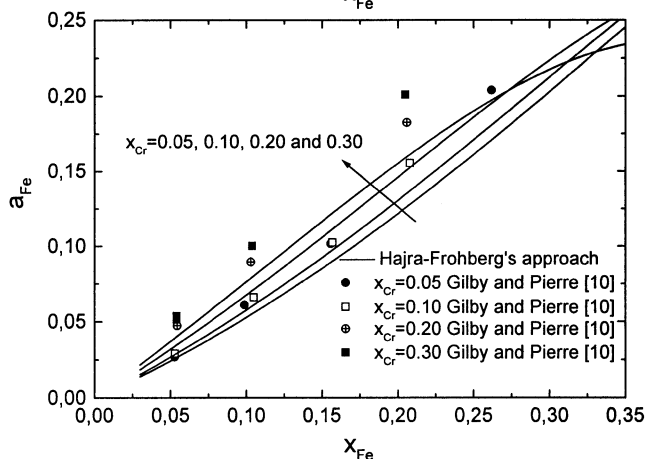
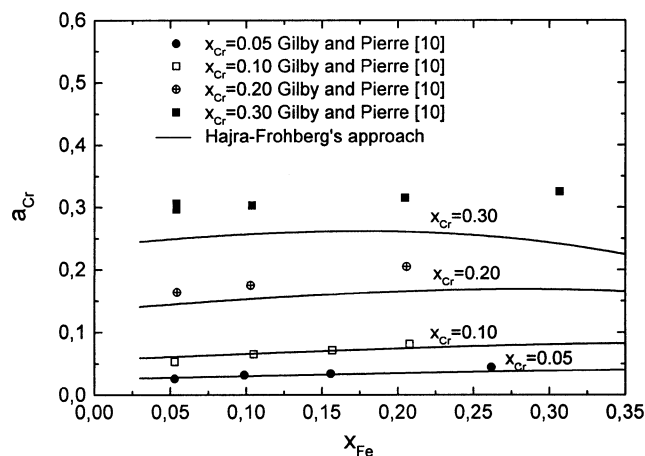
The maximum dissolved Ca in Fe-Cr-Ni melts can also be calculated by the present  $\varepsilon$  approach. Figure 13 shows the calculated and experimental results. It is evident from this figure that the calculated results based on the present  $\varepsilon$  approach are identical to the experimental results.

#### D. Nitrogen in Iron-Based Melts

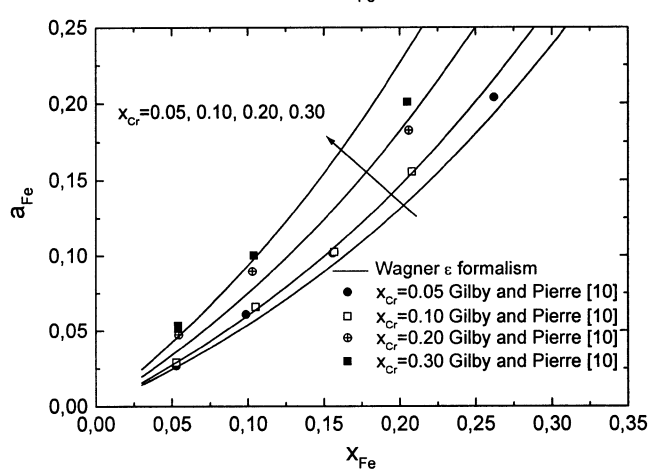
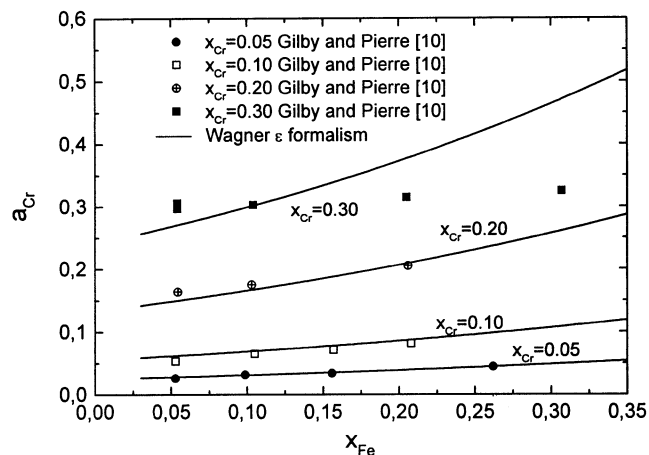
The thermodynamic behavior of nitrogen dissolved in pure liquid iron has been investigated intensively. Table VII gives the equilibrium constant of nitrogen ( $K_N$ ) from different sources. The average value of  $K_N$  at 1873 K of 0.0448 is adopted in the present calculation. Nitrogen dissolved in liquid iron can be expressed as

$$\frac{1}{2} \text{N}_2 = [\text{N}] \quad [40]$$





(c)



(d)

Fig. 2—Continued (c) Comparison of the calculated with experimental results for Ni-Cr-Fe melts at 1873 K (the calculated results are obtained by Hajra-Frohberg's approach). (d) Comparison of the calculated with experimental results for Ni-Cr-Fe melts at 1873 K (the calculated results are obtained by Wagner  $\epsilon$  formalism).

$$\log K_N = \log \frac{h_N}{p_{N_2}^{1/2}} = \log \frac{f_N[\text{pct N}]}{p_{N_2}^{1/2}}$$

At  $p_{N_2} = 1$  bar, the solubility of nitrogen  $[\text{pct N}]_{\text{max}}$  can be deduced from Eq. [40]:

$$\log [\text{pct N}]_{\text{max}} = \log K_N - \log f_N \quad [41]$$

The activity coefficient  $f_i$ , with Henrian 1 pct as the standard state and the activity coefficient  $\gamma_i$  with the pure substance as the standard state, can be converted *via*<sup>[70]</sup>

$$\gamma_i = \gamma_i^0 f_i \left( \frac{M_i}{M_i + 99M_i} \cdot \frac{[\text{pct } i]}{x_i} \right) \quad [42]$$

where  $M_i$  is the atomic weight of element  $i$ . The weight percentage and the mole fraction of component  $i$  are denoted by  $[\text{pct } i]$  and  $x_i$ , respectively.

Wada and Pehlke<sup>[38]</sup> and Ozturk *et al.*<sup>[39]</sup> experimentally determined the solubilities of nitrogen in Fe-Cr melts at 1873 K. Their results are plotted in Figure 14 as compared to the calculated results. Wada and Pehlke's results are based

**Table III. Solubility of C in Fe-*j* Melts at 1823 K<sup>[26]</sup>**

System	[Pct C] <sub>max</sub> (Mass Percentage)	Valid Range
Fe-Cu-C	[pct C] <sub>max</sub> − 0.074 [pct Cu]	[pct Cu] < 3.8
Fe-Sn-C	[pct C] <sub>max</sub> − 0.11 [pct Sn]	[pct Sn] < 4.5
Fe-S-C	[pct C] <sub>max</sub> − 0.40 [pct S]	[pct S] < 0.4
Fe-Ni-C	[pct C] <sub>max</sub> − 0.053 [pct Ni]	[pct Ni] < 8.0
Fe-Cr-C	[pct C] <sub>max</sub> + 0.063 [pct Cr]	[pct Cr] < 9.0
Fe-Mn-C	[pct C] <sub>max</sub> + 0.027 [pct Mn]	[pct Mn] < 25.0
Fe-C	[pct C] <sub>max</sub> = 1.30 + 2.57·10 <sup>−3</sup> <i>T</i> (°C)	1152 °C to 2000 °C

**Table IV.  $\varepsilon_C^j$  and  $\varepsilon_j^i$  in Liquid Iron at 1823 K**

<i>j</i> →	Cu	Sn	S	Ni	Cr	Mn
$\varepsilon_C^j$	4.049	9.628	6.235	2.367	−4.856	−1.884
Reference	25	25	25	25	25	25
$\varepsilon_j^i$	−5.371	−0.294	−5.888	−0.118	−0.105	−0.572
Reference	25	25	25	25	24	23

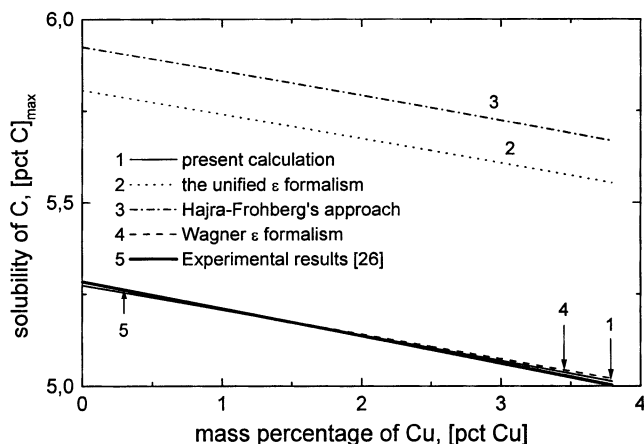


Fig. 3—Solubility of carbon in Fe-Cu melts at 1823 K.

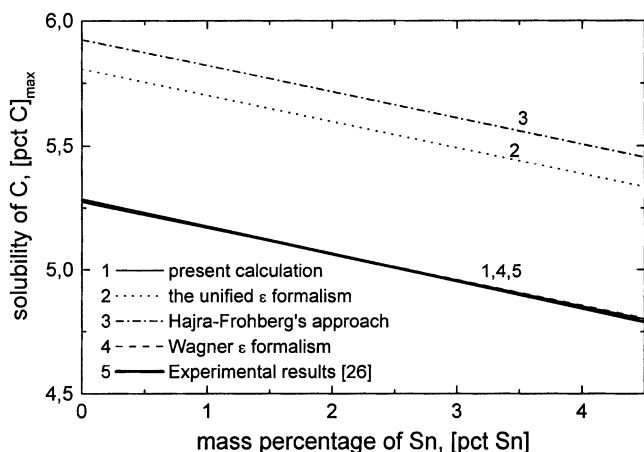


Fig. 4—Solubility of carbon in Fe-Sn melts at 1823 K.

on their experimental data with the second-order approach. It is obvious that the present calculations with only the first-order interaction parameters coincide with the experimental

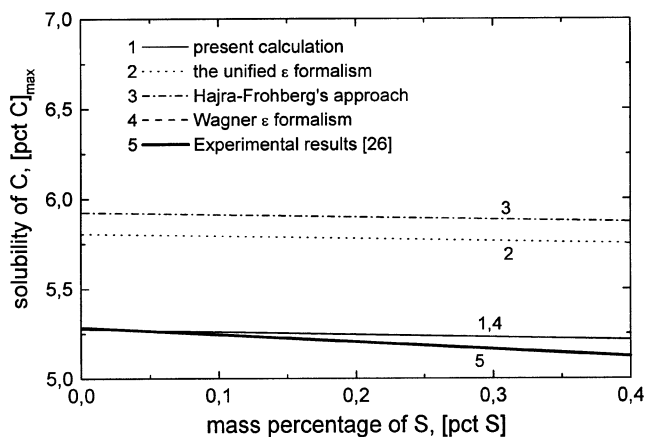


Fig. 5—Solubility of carbon in Fe-S melts at 1823 K.

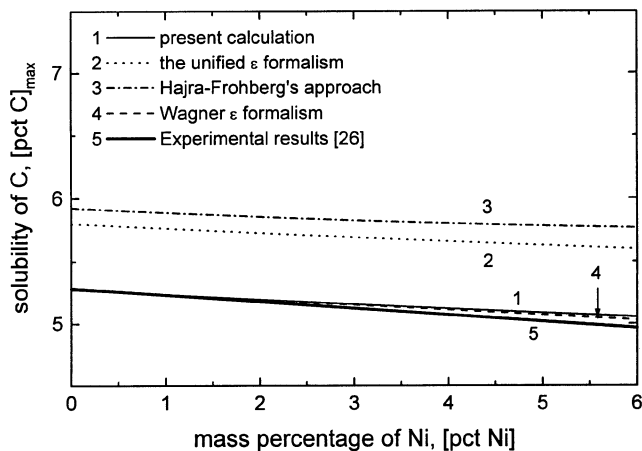


Fig. 6—Solubility of carbon in Fe-Ni melts at 1823 K.

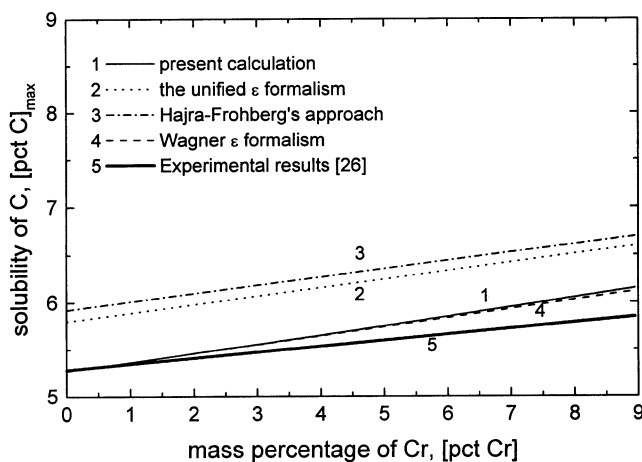


Fig. 7—Solubility of carbon in Fe-Cr melts at 1823 K.

results at low Cr contents. A deviation from experimental data is produced at high Cr contents.

Nitrogen solubilities in Fe-Cr-Ni melts at 1873 K were also measured by Wada and Pehlke.<sup>[38]</sup> Their experimental data of [pct N]<sub>max</sub> vs composition are shown as dashed lines in Figure 15, in which the calculated data are also plotted.

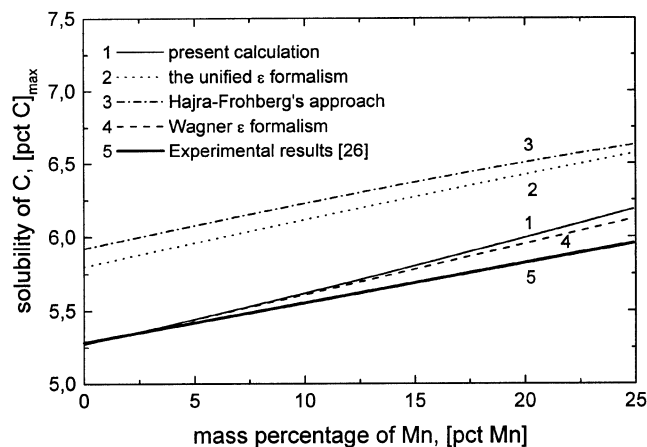


Fig. 8—Solubility of carbon in Fe-Mn melts at 1823 K.

Table V. Presently Used Thermodynamic Parameters in Pure Liquid Iron

	<i>j</i>	References
$e_b^j$	C -0.421	25
	Si -0.131	64
	Ti -1.12	25
	Al -4.09	*
	O -0.17	25
$e_j^i$	N 0	25
	Si 0.103	25
	Ti 0.042	25
	Al 0.043	25
	Cr -0.00067	24
$e_N^j$	Ni 0.0007	25
	Ca -0.002	25
	Mn -0.0026	23
	Mo 0.0121	25
	Cr -0.046	38
$e_{Ni}^j$	Ni 0.0063	38
	Mo -0.011	54
	Mn -0.02	25
	Mo -0.0008	66
	Mn -0.008	25
$e_{Ca}^j$	Cr 0.014	33
	Ni -0.043	33
	Al -0.063	33
	Si -0.096	33
	Mo 0.0018	25
$e_{Cr}^j$	Mn 0.0039	25
	Ni 0.0002	25
	Ni -0.0376	65
	$\gamma_{Ca}^0$ exp (7.6)	35
	oxide $\log k_{M_xO_y}$	
	SiO <sub>2</sub> $-30,110/T + 11.40$	25
	TiO <sub>2</sub> $K = 5 \times 10^{-7}$ at 1873 K	67
	Ti <sub>2</sub> O <sub>3</sub> $-56,060/T + 18.08$	68
	Ti <sub>3</sub> O <sub>5</sub> $-91,304/T + 29.34$	67
	Al <sub>2</sub> O <sub>3</sub> $-64,000/T + 20.57$	25
	Cr <sub>2</sub> O <sub>3</sub> $-43,856/T + 19.55$	24
	CO $-1160/T - 2$	69

\*Average value from different sources.

The calculated results show no difference with the experimental ones at low Cr contents. However, a difference exists between the calculated and experimental results at high Cr

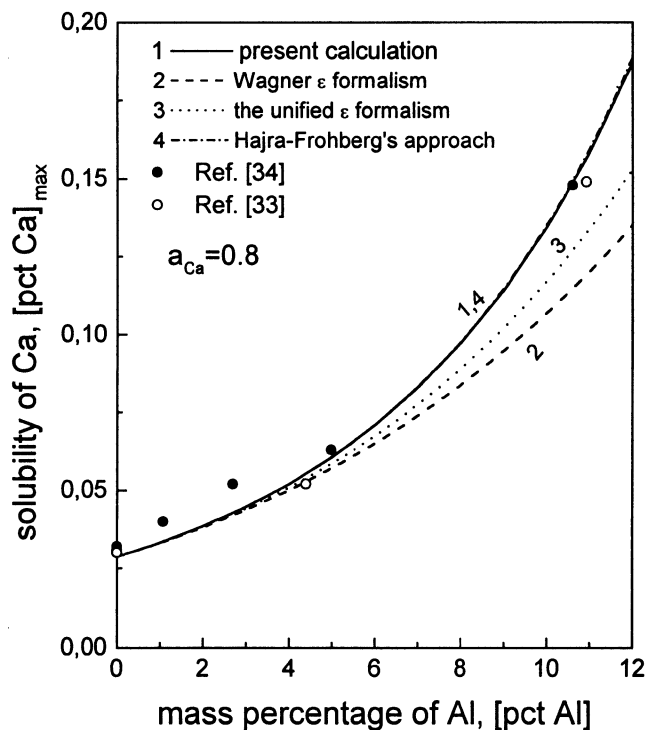


Fig. 9—Ca solubility in Fe-Al melts at 1873 K.

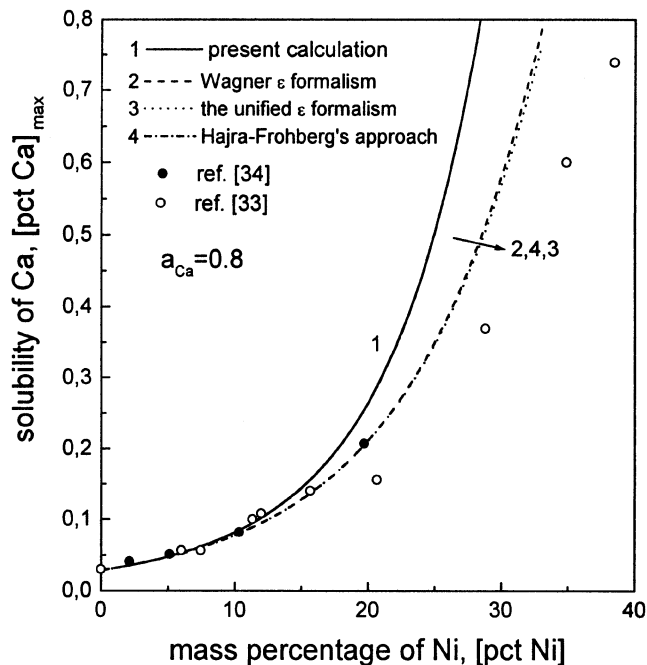


Fig. 10—Ca solubility in Fe-Ni melts at 1873 K.

contents. The difference is caused by the strong interaction between Cr and N. The applicability of the  $\epsilon$  approach to systems with strong interaction between components will be discussed in the following section.

#### E. Oxygen in Iron-Based Melts

The equilibria between deoxidants and oxygen in iron melts have been investigated extensively. The present

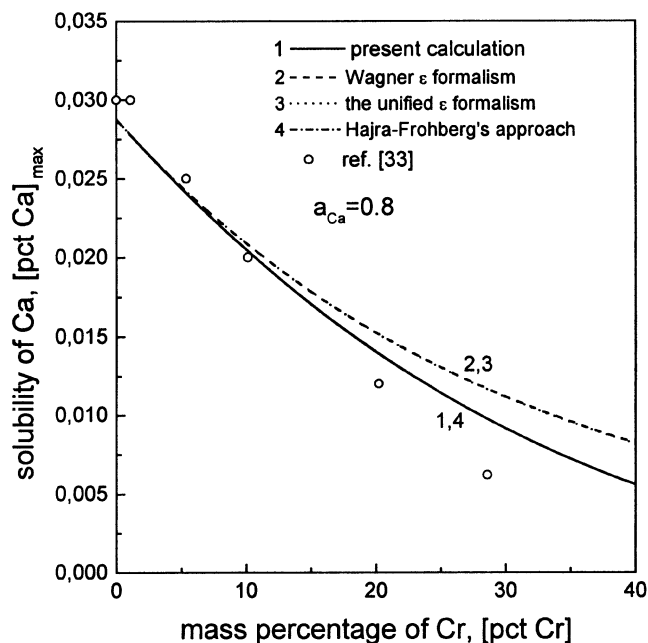


Fig. 11—Ca solubility in Fe-Cr melts at 1873 K.

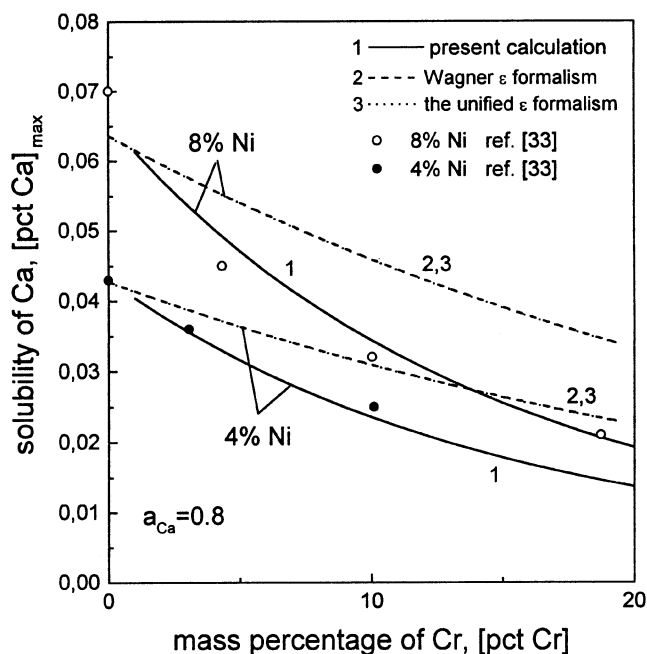


Fig. 13—Ca solubility in Fe-Cr-Ni melts at 1873 K.

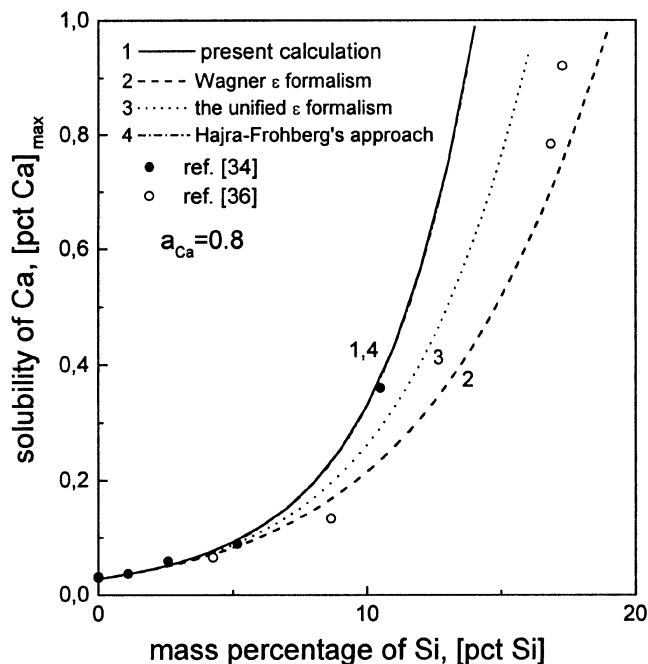


Fig. 12—Ca solubility in Fe-Si melts at 1873 K.

approach was applied to reassess these equilibria. Figure 16 gives the calculated results on the equilibria between oxygen and the elements C, Si, Ti, and Al in iron melts at 1873 K. The presently calculated results agree with the reported results of Turkdogan<sup>[52]</sup> and Gatellier and Olette.<sup>[53]</sup>

## V. EXTENDING THE $\varepsilon$ APPROACH TO SYSTEMS WITH STRONG INTERACTIONS BETWEEN COMPONENTS

The thermodynamic description of concentrated metallic solutions containing strongly interacting components is of

Table VI. Equilibrium between Ca and Iron Melts at 1873 K in a Sealed System<sup>[35]</sup>

System	Fe Phase (Pct) Ca	Ca Phase (Pct)				
		Ca	CaO	Fe	Cr	Ni
Fe	0.030	73	26	0.5 to 1	—	—
Fe-20 pct Cr-10 pct Ni	0.032	69.0	17.9	0.47	0.05	0.66

\*Pct: mass percentage.

importance, from both the practical and theoretical points of view, in performing thermodynamic analyses for metallurgical processes. For concentrated metallic solutions with strongly interacting components, derivatives of the excess Gibbs free energy listed in Table I are no longer constants, such as

$$\frac{1}{RT} \left( \frac{\partial^2 \Delta G^{ex}}{\partial x_j^2} \right)_{x_1 \rightarrow 1} = \varepsilon_j^j + \sum_{i=2}^N \rho_j^{ji} x_i \quad [43]$$

$$\frac{1}{RT} \left( \frac{\partial^2 \Delta G^{ex}}{\partial x_k \partial x_j} \right)_{x_1 \rightarrow 1} = \varepsilon_k^j + \sum_{i=2}^N \rho_k^{ji} x_i \quad [44]$$

Therefore, Eqs. [23] and [24] become more general, to describe the thermodynamics of concentrated metallic solutions after replacing  $\varepsilon_i^l$  and  $\varepsilon_i^t$  by  $\varepsilon_i^l + \sum_{j=2}^N \rho_i^{lj} x_j$  and  $\varepsilon_i^t + \sum_{j=2}^N \rho_i^{tj} x_j$ , respectively, where  $l$  and  $t$  represent solutes and  $\rho$  represents the second-order interaction parameters on the basis of mole fraction;  $\rho_i^{ji} = \rho_i^{ji}$ ; and  $\rho_i^{jk} \neq 0$  for strong interaction between the elements  $j$ ,  $k$ , and  $i$  at concentrated levels. Otherwise, at dilute levels or in systems without a strong interaction between elements,  $\rho$  is neglected in the present  $\varepsilon$  approach.

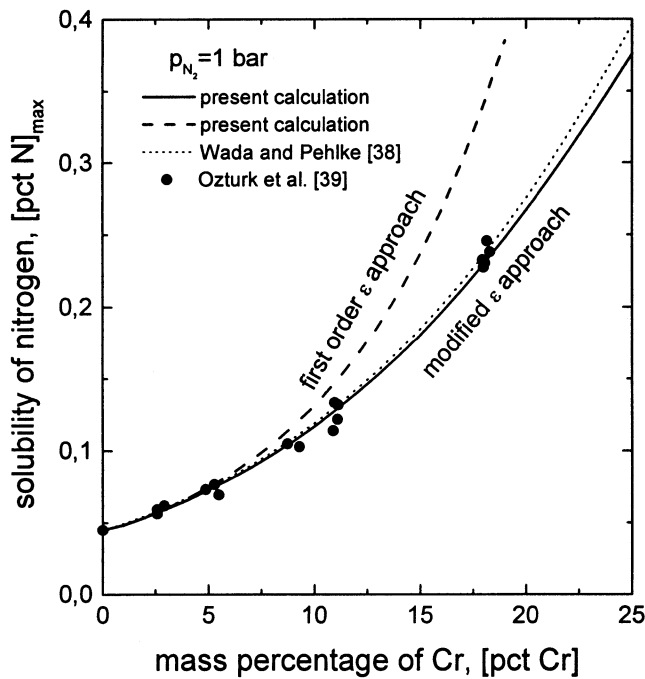


Fig. 14—Nitrogen solubility in Fe-Cr melts at 1873 K.

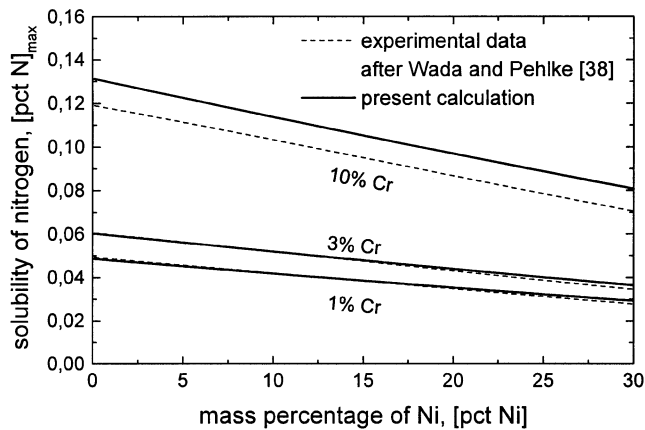


Fig. 15—The calculated and experimental values of nitrogen solubilities in Fe-Cr-Ni melts at 1873 K.

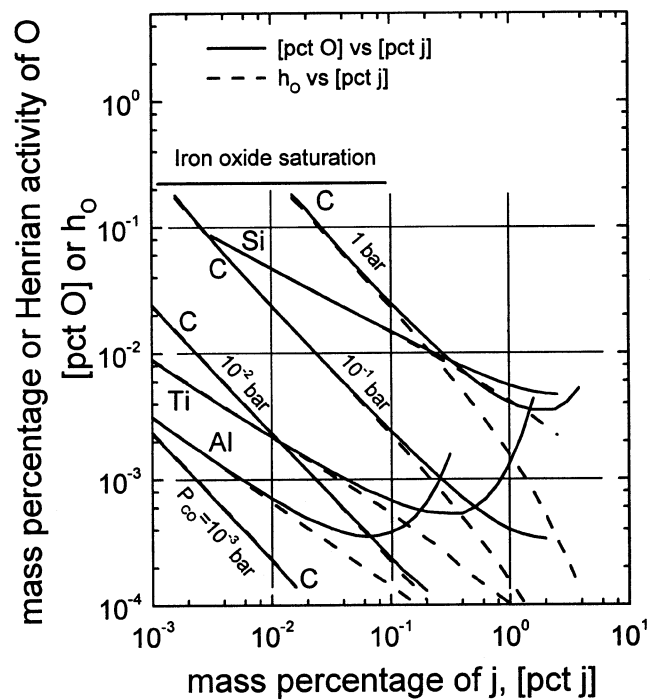


Fig. 16—The calculated results on equilibrium between oxygen and the elements C, Si, Ti, and Al in iron at 1873 K.

#### A. Nitrogen in Iron-Based Melts

Figure 14 schematically shows the experimental and calculated results. It is obvious that the first-order approach deviates from experimental results at high Cr contents. Modification of the interaction parameter  $\epsilon_N^{\text{Cr}}$  is introduced, and  $r_N^{\text{Cr}} = 0.00045$  is obtained after optimization. The calculated results using the modified  $\epsilon$  approach are identical with experimental results at both low and high Cr contents. Nitrogen solubilities in Fe-Cr-Ni melts at 1873 K are calculated on the basis of the modified  $\epsilon$  approach. Figure 17 demonstrates the calculated and experimental results. More calculations are performed for Fe-Cr-Ni-Mo and Fe-Cr-Ni-Mn melts at 1873 K, and the calculated results are plotted in Figures 18 through 21, respectively, comparing experimental data. It is obvious that the calculations show no difference with the experimental results.

Table VII. Equilibrium Constant of the Reaction  $\text{N}_2 = [\text{N}]$  in Pure Liquid Iron

Authors	Reference	Year	$\text{Log } K_N = \text{Log } (h_N/p_{\text{N}_2}^{1/2})$	$p_{\text{N}_2}$ (Bar)	Method
Parlee and Kashyap	41	1958	$-665/T - 1.00$	0.06 to 1.00	Sieverts
Schenck <i>et al.</i>	42	1959	$-767/T - 0.95$	0.13 to 1.00	sampling
Humbert and Elliot	43	1960	$-225/T - 1.218$	0.25 to 1.10	Sieverts
Turnock and Pehlke	44	1966	$-276/T - 1.20$	0.40 to 1.00	Sieverts
Gomersall <i>et al.</i>	45	1968	$-285/T - 1.21$	1.00	levitation
Wada and Pehlke	38	1977	$-247/T - 1.22$	1.00	calculation
Morita and Kunisada	46	1977	$-941/T - 0.841$	1.00	sampling
Turkdogan	47	1980	$-188/T - 1.248$	1.00	calculation
Wada and Pehlke	48	1981	$-226/T - 1.216$	1.00	Sieverts
Schürmann <i>et al.</i>	40	1981	$-297/T - 1.198$	1.00	Sieverts
Ishii <i>et al.</i>	49	1982	$-400/T - 1.126$	0.05 to 1.01	Sieverts
			$-518/T - 1.063$	0.05 to 1.01	sampling
Wada <i>et al.</i>	50	1986	$-430/T - 1.125$	1.00	levitation
Wu and Janke	51	1996	$-247/T - 1.22$ (Fe-Cr melts)	1.00	selected
			$-285/T - 1.21$ (Fe-C melts)	1.00	selected

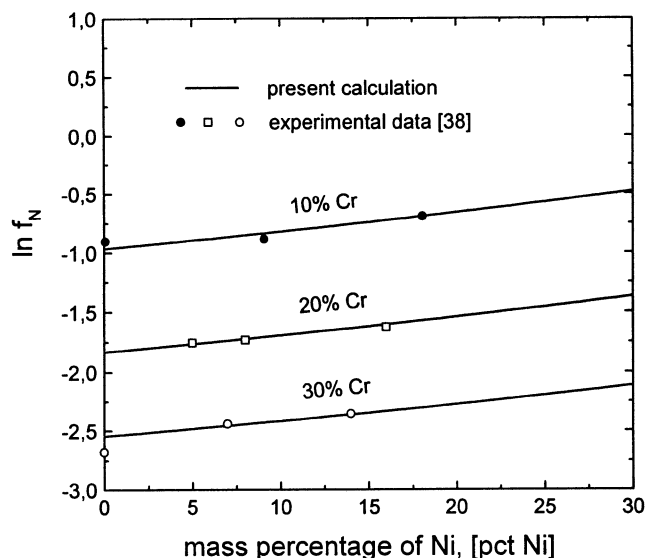


Fig. 17—Calculated and experimental values of  $\ln f_N$  against [pct Ni] in Fe-Cr-Ni melts at 1873 K.

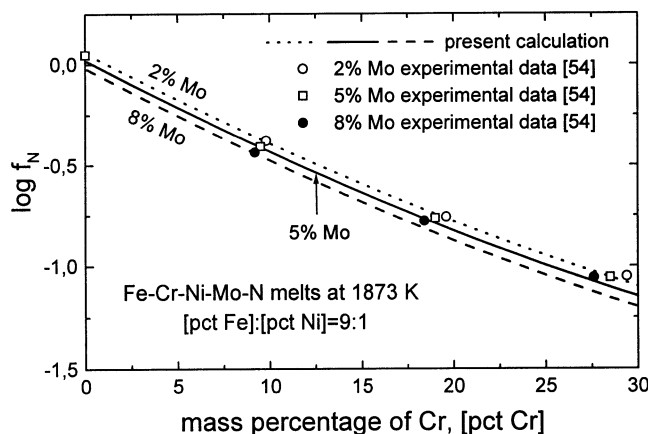


Fig. 18—Calculated and experimental values of  $\log f_N$  in Fe-Cr-Ni-Mo melts at 1873 K.

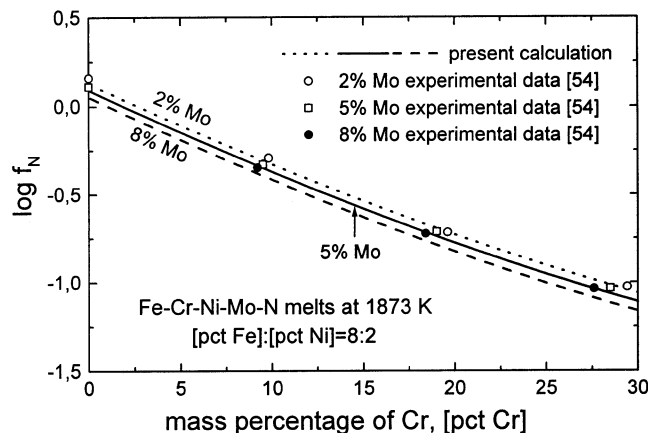


Fig. 19—Calculated and experimental values of  $\log f_N$  in Fe-Cr-Ni-Mo melts at 1873 K.

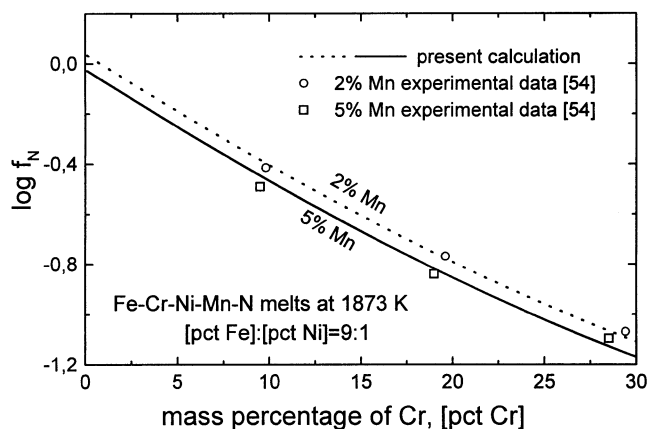


Fig. 20—Calculated and experimental values of  $\log f_N$  in Fe-Cr-Ni-Mn melts at 1873 K.

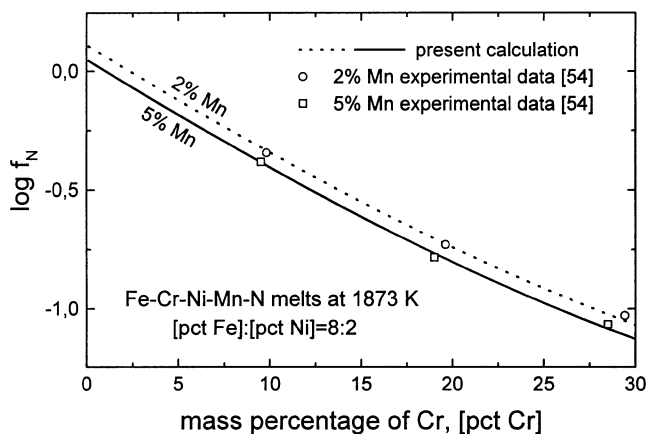


Fig. 21—Calculated and experimental values of  $\log f_N$  in Fe-Cr-Ni-Mn melts at 1873 K.

## B. Oxygen in Iron-Based Melts

Figure 22 shows the comparison of the calculated and experimental results for Fe-Cr-O melts at 1873 K. The term  $e_O^{\text{Cr}} = -0.055$ ,<sup>[25]</sup> and  $r_O^{\text{Cr}}$  is obtained as 0.00073 from fitting the experimental data as shown in Figure 22. The Al-O equilibrium in liquid iron was intensively studied. The value of  $e_O^{\text{Al}}$  in an infinitely dilute liquid iron and at 1873 K was reported to show a little difference, such as  $-4.09$ ,<sup>[55]</sup>  $-3.9$ ,<sup>[56]</sup>  $-4.60$ ,<sup>[58]</sup>  $-5.25$ ,<sup>[62]</sup>  $-5.25$ ,<sup>[63]</sup> and  $-1.17$ .<sup>[25]</sup> The average of  $-4.09$  is taken as the value  $e_O^{\text{Al}}$  in an infinitely dilute liquid iron and at 1873 K. The value of  $r_O^{\text{Al}} = 2.67$ , reported by Seo *et al.*,<sup>[55]</sup> is taken in the present calculation. Figures 23 and 24 compare the calculated and experimental results. A good agreement between them is reached at both low and high Al contents. The modified  $\varepsilon$  approach is applied to the Fe-Cr-Ni-Al-O melts. The calculated results, together with experimental results, are plotted in Figure 25. It is evident that the calculated results are identical to the experimental ones. In the calculation,  $e_{\text{Al}}^{\text{Cr}}$  is evaluated according to Eq. [45], which was deduced from experimental data by Janke and Fischer.<sup>[61]</sup>

$$2e_{\text{Al}}^{\text{Cr}} + e_{\text{Al}}^{\text{Ni}} = -\frac{1}{3} \log K_{\text{Al}_2\text{O}_3} + 4.715 \quad [45]$$

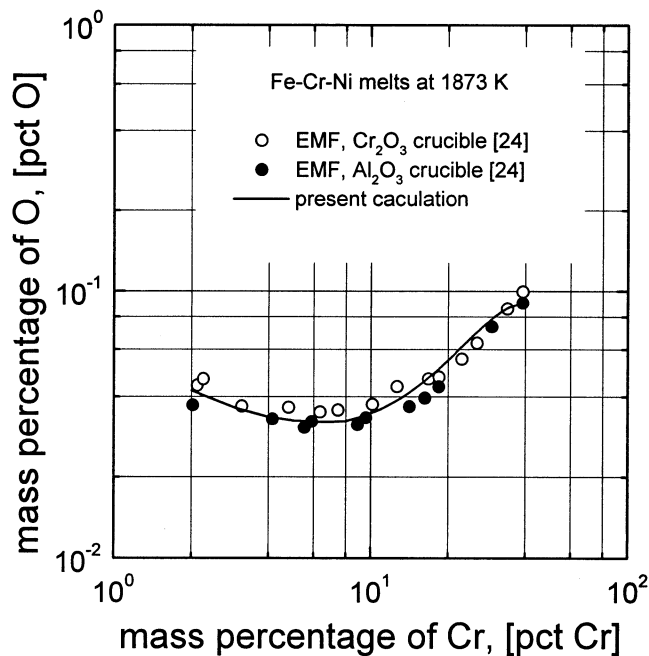


Fig. 22—Oxygen solubilities in  $\text{Cr}_2\text{O}_3$ -saturated Fe-Cr-O melts at 1873 K.

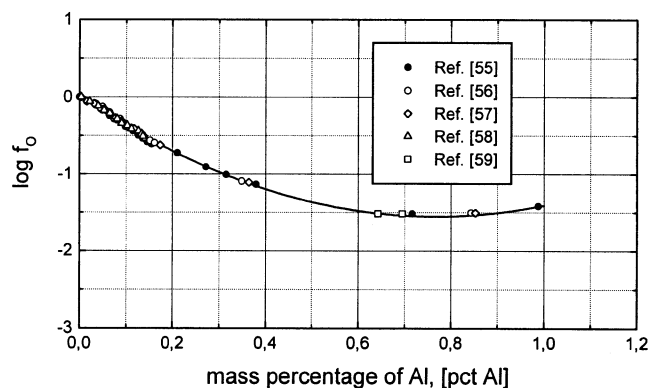


Fig. 23—Activity coefficient of oxygen in  $\text{Al}_2\text{O}_3$ -saturated Fe-Al-O melts at 1873 K.

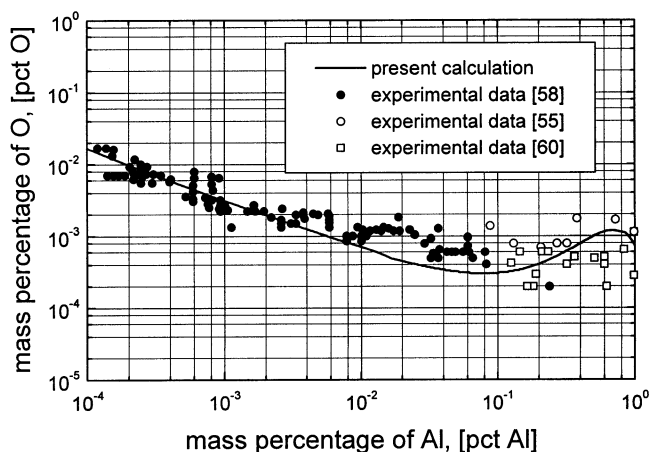


Fig. 24—The equilibrium of Al and O in  $\text{Al}_2\text{O}_3$ -saturated Fe-Al-O melts at 1873 K.

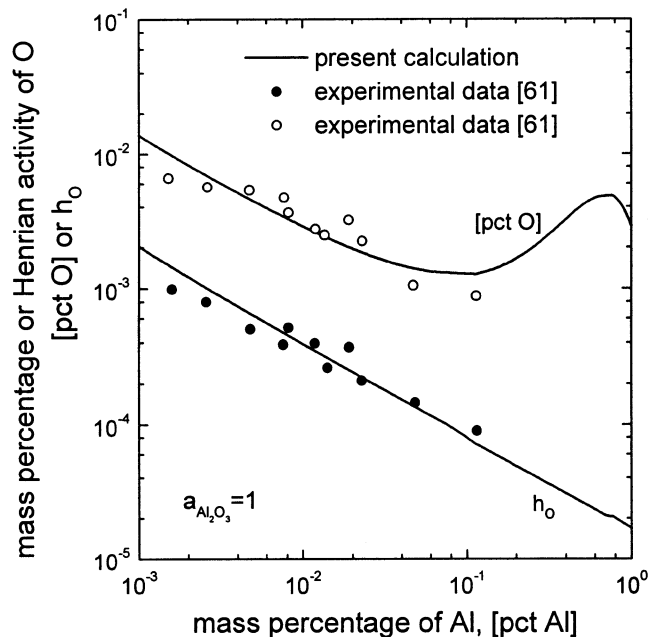


Fig. 25—Comparison of the calculated with experimental results on the Al-O equilibrium in Fe-20 pct Cr-10 pct Ni melts 1873 K.

where  $e_{\text{Al}}^{\text{Cr}}$  equals 0.033 after inserting the values of  $K_{\text{Al}_2\text{O}_3}$  and  $e_{\text{Al}}^{\text{Ni}}$  from Table V.

## VI. CONCLUSIONS

Calculation of the activity coefficients of a solvent and solutes in a multicomponent metallic solution is important in performing thermodynamic analyses for metal-making processes. For a dilute metallic solution, the logarithm of the activity coefficients of the solutes normally shows a linear relation with composition. The first-order Wagner  $\epsilon$  formalism successfully describes the thermodynamics of dilute metallic solutions. However, the logarithm of the activity coefficients of solutes in a concentrated metallic solution is no longer a linear function of composition. The presently developed  $\epsilon$  approach is suitable for calculating the activity coefficients of a solvent and solutes in multicomponent metallic solutions at both dilute and concentrated levels. It is thermodynamically consistent with the Gibbs–Duhem equation and the other thermodynamic relations. It may be concluded, after comparison of the calculated and experimental results, that the present  $\epsilon$  approach is reliable and gives more accurate results. The modified  $\epsilon$  approach successfully describes the thermodynamics of systems with strong interactions between components at dilute and concentrated levels.

## NOMENCLATURE

- $\gamma_1$  Raoultian activity coefficient of the solvent in a metallic solution, on the basis of the mole fraction (pure substance standard)
- $\gamma_i$  Raoultian activity coefficient of solute  $i$  in a metallic solution, on the basis of the mole fraction (pure substance standard)

$\gamma_i^0$	Raoultian activity coefficient of solute $i$ at an infinite dilution of solution, on the basis of the mole fraction
$\varepsilon_i^i$	the first-order self-interaction parameter of $i$ , on the basis of the mole fraction
$\varepsilon_i^j$	the first-order interaction parameter of $j$ upon $i$ , on the basis of the mole fraction
$\rho_i^j$	the second-order interaction parameter of $j$ upon $i$ , on the basis of the mole fraction
$\rho_i^{jk}$	the second-order interaction parameter of $j$ and $k$ upon $i$ , on the basis of the mole fraction
$\alpha_{ij}$	Darken interaction parameter between $i$ and $j$
$\varepsilon_{ij}$	Pelton and Bale interaction parameter between $i$ and $j$ , on the basis of the mole fraction
$\varepsilon_{jkl}$	Pelton and Bale interaction parameter between $j$ , $k$ , and $l$ , on the basis of the mole fraction
$\varepsilon_{jklm}$	Pelton and Bale interaction parameter between $j$ , $k$ , $l$ , and $m$ , on the basis of the mole fraction
$e_i^i$	the first-order self-interaction parameter of $i$ , on the basis of the mass percentage
$e_i^j$	the first-order interaction parameter of $j$ upon $i$ , on the basis of the mass percentage
$r_i^j$	the second-order interaction parameter of $j$ upon $i$ , on the basis of the mass percentage
$r_i^{jk}$	the second-order interaction parameter of $j$ and $k$ upon $i$ , on the basis of the mass percentage
$\Phi_{nmkj}\dots$	Maglues polynomial-constant coefficients
$\Delta G^{ex}$	molar excess Gibbs free energy
$f_i$	Henrian activity coefficient of solute $i$ in a metallic solution
$a_i$	Raoultian activity of element $i$ in a metallic solution
$h_i$	Henrian activity of element $i$ in a metallic solution
$f_i$	fugacity of element $i$ in a metallic solution
$f_i^0$	fugacity of element $i$ in its pure standard state
$K_N$	equilibrium constant of the reaction $1/2N_2 = [N]$ in pure liquid iron
$K_{M_xO_y}$	equilibrium constant of the reaction $x[M] + y[O] = (M_xO_y)$ in pure liquid iron
$p_i$	partial pressure of element $i$ in a metallic solution
$p_i^0$	partial pressure of element $i$ in its pure standard state
$w_{ij}$	energy parameter between $i$ and $j$
$u_{ij}$	pair potential energy
$z$	coordination number
$x_i$	mole fraction of element $i$ in a metallic solution
[pct $i$ ]	mass percentage of element $i$ in a metallic solution
[pct $i$ ] <sub>max</sub>	solubility of element $i$ in a metallic solution
$M_i$	atomic weight of element $i$
$N_A$	Avogadro number
$R$	universal gas constant
$T$	absolute temperature

## REFERENCES

1. C. Wagner: *Thermodynamics of Alloys*, Addison-Wesley Press, Cambridge, MA, 1952, pp. 51-53.
2. C.H.P. Lupis and J.F. Elliott: *Acta Metall.*, 1966, vol. 14, pp. 529-38.
3. L.S. Darken: *TMS-AIME*, 1967, vol. 239, pp. 80-89.
4. S. Srikanth and K.T. Jacob: *Metall. Trans. B*, 1988, vol. 19B, pp. 269-75.
5. A.D. Pelton and C.W. Bale: *Metall. Trans. A*, 1986, vol. 17A, pp. 1211-15.
6. S. Srikanth and K.T. Jacob: *Trans. Iron Steel Inst. Jpn.* 1989, vol. 29, pp. 171-74.
7. C.H.P. Lupis: *Acta Metall.*, 1966, vol. 14, pp. 1029-32.
8. C.W. Bale and A.D. Pelton: *Metall. Trans. A*, 1990, vol. 21A, pp. 1997-2002.
9. M. Margules: *Sitz-Ber. Math.-Naturw. Kl. Bayer. Akad. Wiss.*, München IIa, 1895, vol. 104, p. 1243
10. S.W. Gilby and G.R. St. Pierre: *TMS-AIME*, 1969, vol. 245, pp. 1749-58.
11. J.P. Hajra and M.G. Froberg: *Metall. Trans. B*, 1992, vol. 23B, pp. 23-28.
12. J.P. Hajra and M.G. Froberg: *Steel Res.*, 1989, vol. 60, pp. 479-84.
13. J.P. Hajra, S.R. Reddy, and M.G. Froberg: *Metall. Mater. Trans. B*, 1995, vol. 26B, pp. 495-502.
14. A.D. Pelton: *Metall. Mater. Trans. B*, 1997, vol. 28B, pp. 869-76.
15. M. Shimoji and T. Itami: *Non-Metallic Elements in Liquid Metals*, Trans Tech Publications Ltd., Switzerland, 1996, pp. 15-27 and 60-181.
16. L. Pauling: *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, NY, 1960.
17. M. Shimoji and N. Niwa: *Acta Metall.*, 1957, vol. 5, pp. 496-501.
18. J.H. Hildebrand and R.L. Scott: *Solubility of Non-Electrolytes*, Reinhold, New York, NY, 1950.
19. B.W. Mott: *Phil. Mag.*, 1957, vol. 2, p. 259.
20. T. Tanaka, N.A. Gocken, P.J. Spencer, Z. Morita, and T. Iidea: *Z. Metallkd.*, 1993, vol. 84, pp. 100-05.
21. S. Ueno, Y. Waeda, K.T. Jacob, and S. Tamaki: *Steel Res.*, 1998, vol. 59, pp. 474-83.
22. F. Wang, X. Li, Q. Han, and N.X. Zhang: *Metall. Mater. Trans. B*, 1997, vol. 28B, pp. 109-13.
23. Z. Ma and D. Janke: *Acta Metall. Sinica*, 1999, vol. 12, pp. 127-36.
24. S. Dimitrov, H. Wenz, K. Koch, and D. Janke: *Steel Res.*, 1995, vol. 66, pp. 39-44.
25. *Steelmaking Data Sourcebook*, The Japan Society for the Promotion of Science and The 19th Committee on Steelmaking, Revised edition, Gordon and Breach Science Publishers, 1988, pp. 280-96.
26. F. Neumann and H. Schenck: *Arch. Eisenhüttenwes.*, 1959, vol. 30, pp. 477-83.
27. J. Chipman: *J. Iron Steel Inst.*, 1955, vol. 181, p. 97.
28. A. Ueda, K. Fujimura, and T. Mori: *Tetsu-to-Hagané*, 1975, vol. 61, p. 2962.
29. J. Chipman: *Metall. Trans.*, 1970, vol. 1, pp. 2163-68.
30. T. Mori, K. Fujimura, H. Okajima, and A. Yamanouchi: *Tetsu-to-Hagané*, 1968, vol. 54, p. 321.
31. B.I. Burylev: *Izv. Vuzov. Cher. Met.*, 1961, vol. 10, pp. 5-11.
32. H. Schenck, M.G. Froberg, E. Steinmetz, and B. Rutenberg: *Arch. Eisenhüttenwes.*, 1962, vol. 33, pp. 223-27.
33. M. Köhler, H.-J. Engell, and D. Janke: *Steel Res.*, 1985, vol. 56, pp. 419-23.
34. D.L. Sponseller and R.A. Flinn: *TMS-AIME*, 1964, vol. 230, pp. 876-88.
35. M. Breitzmann, H.-J. Engell, and D. Janke: *Steel Res.*, 1988, vol. 59, pp. 289-94.
36. H.-J. Engell, M. Köhler, H.-J. Fleischer, R. Tielmann, and E. Schürmann: *Stahl Eisen*, 1984, vol. 104, pp. 443-90.
37. B. Song and Q. Han: *Metall. Mater. Trans. B*, 1998, vol. 29B, pp. 415-20.
38. H. Wada and R.D. Pehlke: *Metall. Trans. B*, 1977, vol. 8B, pp. 443-50.
39. B. Ozturk, R. Matway, and R.J. Fruehan: *Metall. Mater. Trans. B*, 1995, vol. 26B, pp. 563-68.
40. E. Schürmann and W. Kattlitz: *Arch. Eisenhüttenwes.*, 1981, vol. 52, pp. 219-24 and 253-60.
41. N. Parlee and V.C. Kashyap: *Trans. TMS-AIME*, 1958, vol. 212, p. 86.
42. H. Schenck, M.G. Froberg, and H. Graf: *Arch. Eisenhüttenwes.*, 1959, vol. 30, pp. 533-37.
43. J.C. Humbert and J.F. Elliott: *TMS-AIME*, 1960, vol. 218, pp.1076-87.
44. P.H. Turnock and R.D. Pehlke: *TMS-AIME*, 1966, vol. 236, pp. 1541-47.
45. D.W. Gomersall, A. McLean, and R.G. Ward: *TMS-AIME*, 1968, vol. 242, pp. 1309-15.
46. Z. Morita and K. Kunisada: *Tetsu-to-Hagané*, 1977, vol. 63, pp. 1663-71.
47. E.T. Turkdogan: *Physical Chemistry of High Temperature Technology*, Academic Press, New York, NY, 1980, pp. 5-24.



48. H. Wada and R.D. Pehlke: *Metall. Trans. B*, 1981, vol. 12B, pp. 333-39.
49. F. Ishii, S. Ban-Ya, and T. Fuwa: *Tetsu-to-Hagané*, 1982, vol. 68, pp. 946-55.
50. H. Wada, S.W. Lee, and R.D. Pehlke: *Metall. Trans. B*, 1986, vol. 17B, pp. 238-39.
51. P.W. Wu and D. Janke: *Ironmaking and Steelmaking*, 1996, vol. 23, pp. 247-54.
52. E.T. Turkdogan: *Arch. Eisenhüttenwes.*, 1983, vol. 54, pp. 1-10.
53. C. Gatellier and M. Olette: *Rev. Met.*, 1979, vol. 76, pp. 377-86.
54. H. Wada and R.D. Pehlke: *Metall. Trans. B*, 1977, vol. 8B, pp. 675-82.
55. J.D. Seo, S.H. Kim, and K.R. Lee: *Steel Res.*, 1998, vol. 69, pp. 49-53.
56. R.J. Fruehan: *Metall. Trans.*, 1970, vol. 1, pp. 3403-10.
57. H. Suito, H. Inoue, and R. Inoue: *Iron Steel Inst. Jpn. Int.*, 1991, vol. 31, pp. 1381-88.
58. S. Dimitrov, A. Weyl, and D. Janke: *Steel Res.*, 1995, vol. 66, pp. 3-7.
59. L.E. Rhode, A. Choudhury, and M. Wahlster: *Arch. Eisenhüttenwes.*, 1971, vol. 42, pp. 165-74.
60. D. Janke and W.A. Fischer: *Arch. Eisenhüttenwes.*, 1976, vol. 47, pp. 195-98.
61. D. Janke and W.A. Fischer: *Arch. Eisenhüttenwes.*, 1976, vol. 47, pp. 589-94.
62. A. McLean and H.B. Bell: *J. Iron Steel Inst.*, 1965, vol. 203, pp. 123-30.
63. S. Gustafsson and P.O. Mellberg: *Scand. J. Metall.*, 1980, vol. 9, pp. 111-16.
64. G.K. Sigworth and J.F. Elliott: *Met. Sci.*, 1974, vol. 8, pp. 298-310.
65. S.W. Cho and H. Suito: *Steel Res.*, 1995, vol. 66, pp. 237-43.
66. F. Wang, X. Li, Q. Han, and N. Zhang: *Metall. Trans. B*, 1997, vol. 28B, pp. 109-13.
67. B. Deo and R. Room: *Fundamentals of Steelmaking Metallurgy*, Prentice-Hall International, New York, NY, 1993, p. 53.
68. *Iron and Steel Handbook*, 3rd ed., ISIJ, Maruzen Co. Ltd., Tokyo, 1981, vol. 1, p. 15.
69. F. Oeters: *Metallurgy of Steelmaking*, Verlag Stahleisen mbH, Düsseldorf, 1994, p. 17.
70. S. Wei: *Thermodynamics of Process Metallurgy*, Shanghai Science and Technology Press, Shanghai, 1980, pp. 385-87.